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Novel Tools for Water Quality Monitoring –
From Field to Laboratory



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Institute of Chemistry, Faculty of Science and Technology, University of Tartu.

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I LIST OF ORIGINAL PUBLICATIONS

The thesis is based on the following articles which are referred to by their Roman numerals:

- I. **Näykki T**, Virtanen A, Leito I, Software support for the Nordtest method of measurement uncertainty evaluation, *Accredit Qual Assur*, **2012**, 17 (6):603–612
- II. **Näykki T**, Magnusson B, Helm I, Jalukse L, Väisänen T, Leito I, Comparison of measurement uncertainty estimates using quality control and validation data, *J Chem Metrol*, **2014**, 8 (1): 1–12
- III. **Näykki T**, Virtanen A, Kaukonen L, Magnusson B, Väisänen T, Leito I, Application of the Nordtest method for real-time uncertainty estimation of on-line field measurement, submitted to *Environ Monit Assess*
- IV. **Näykki T**, Jalukse L, Helm I, Leito I, Dissolved oxygen concentration interlaboratory comparison: What can we learn?, *Water*, **2013**, 5:420–442.
- V. **Näykki T**, Leivuori M, Björklöf K, Väisänen R, Laine M, Väisänen T, Leito I, Proficiency test of pH, conductivity and dissolved oxygen concentration field measurements in river water, *Accredit Qual Assur*, **2014**, DOI 10.1007/s00769-014-1064-5
- VI. **Näykki T**, Koponen S, Väisänen T, Pyhälähti T, Toivanen T, Leito I, Validation of a new measuring system for water turbidity field measurements, *Accredit Qual Assur*, **2014**, 19 (3):175–183
- VII. **Näykki T**, Sara-Aho T, Väisänen T, Leito I, Application of enriched stable Hg-196 isotope for monitoring the stability of total mercury in water samples, submitted to *Int J Environ Anal Chem*
- VIII. **Näykki T**, The use of silylation for minimizing the interference effects caused by contamination in ultra-low level mercury analytics. *Anal Bioanal Chem*, **2002**, 372 (7): 829–831

Author's contribution

- Paper I: Main person responsible for planning and writing the manuscript. Participated in designing the MUKIT software. Participated in conducting the survey and handling the data.
- Paper II: Main person responsible for planning and writing the manuscript. Performed all the experimental work.

- Paper III: Main person responsible for planning and writing the manuscript. Participated in designing the automated measuring system and the AutoMUKit software.
- Paper IV: Wrote large part of the text focusing on the processing of the data, comparison of the analytical methods and the aspects of improving the quality of the dissolved oxygen measurement results.
- Paper V: Main person responsible for planning and writing the manuscript. Participated in organising the proficiency test.
- Paper VI: Main person responsible for planning and writing the manuscript. Performed majority of the experimental work with the validated device.
- Paper VII: Main person responsible for planning and writing the manuscript. Planned the stability study protocol.
- Paper VIII: Main person responsible for planning and writing the manuscript. Performed all the experimental work.

2 ABBREVIATIONS

bias	Estimate of a systematic measurement error
BSD	Berkeley Software Distribution
ca.	circa (approximately)
CITAC	Co-operation on International Traceability in Analytical Chemistry
CoDeSys	Controller Development System
CRM	Certified Reference Material
DO	Dissolved Oxygen
e.g.	exempli gratia (for example)
E_n	Describes the performance of participant in proficiency test
etc.	Et cetera (and other things)
EU	European Union
FEP	Perfluoroethene-propene
FNU	Formazine Nephelometric Unit
GDP	Gross Domestic Product
GPS	Global Positioning System
GUM	The Guide to the Expression of Uncertainty in Measurement
i.e.	id est (that is)
IEC	International Electrotechnical Commission
ILC	Interlaboratory Comparison
In situ	Operation or procedure that is performed on the sampling site
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
k	Coverage factor
Lab	Laboratory
LIMS	Laboratory Information Management System
LOQ	Limit of Quantification
MA	Measurement application
MUkit	Measurement Uncertainty kit (software package)
MySQL	Open-source relational database management system
OECD	Organisation for Economic Cooperation and Development
PhpMySQLAdmin	Software tool intended to handle the administration of MySQL over the Web
PT	Proficiency Test
PTFE	Polytetrafluoroethene
QMS	Quality Management System
QUAM	Quantifying Uncertainty in Analytical Measurement
SI	International System of Units
s_R	Reproducibility standard deviation

SQL	Structured Query Language
SYKE	Finnish environment institute
U	Expanded measurement uncertainty
u_{bias}	Uncertainty component for method and laboratory bias
u_{c}	Combined standard uncertainty
u_{cref}	Standard uncertainty of the reference value (of the CRM)
u_{Rw}	Uncertainty component for reproducibility within-laboratory (intermediate precision)
VIM	International Vocabulary of Basic and General Terms in Metrology
Wlan	Wireless local area network

3 INTRODUCTION

Internationally, the comparability of measurement results is remarkably important both to decision makers and the business community and the matter is of great economic importance. A vast number of important decisions – many of them industrial or environment-related – are based on measurement results.

In 2002 it was estimated that Europe spends more than €80 billion per year, or nearly 1 % of the EU's GDP, on measurement activity from directly quantifiable sources alone [1]. Approximately 40 % of the European Union's directives involve measurements [2]. Many of these are related to the environmental sector, including quality of water. The Organization for Economic Cooperation and Development (OECD) has estimated that about 80 percent of global merchandise trade is affected by standards or by regulations that embody standards [3]. All these figures reveal that measurement results are important factors both for decision-making processes and for fluent international trading.

The reliability and comparability of the analytical results can be improved by realistic uncertainty estimates and by ensuring the traceability of analytical results. The knowledge of the magnitude of the measurement uncertainty related to the measurement result is also a key factor for comparability of the laboratories and the quality they are able to achieve. There are several guides and standards dealing with estimation of measurement uncertainty [4–9], but for many routine laboratories this task is laborious and intellectually challenging. The need for assisting tools has been apparent [I, II].

The state of surface waters and its development interests citizens and authorities. The state of waters is monitored in European Union from the perspectives of water resources management, environmental protection and environmental awareness. Throughout the EU the national water regulations are quite similar as they all need to comply with the EU regulations for water policy [10, 11]. Water resources management carried out under the EU's water policy and national acts on water resource management require knowledge of the chemical and ecological state of waters and measures for achieving good water status. In order to assess the development of the state of waters, monitoring must be arranged with a system that ensures the high quality of monitoring and the application of consistent methods in the river basin districts [10, 11].

Chemical monitoring of the water bodies are usually carried out using standardised methods ensuring the high quality and comparability of the results to fulfill national water regulations [12]. On the other hand, there is a global trend in monitoring measurements to move away from standard-based requirements and towards performance-based requirements. Performance-based requirements allow using non-standardised methods that are validated and proved to produce reliable measurement results [13, 14]. Pressures to streamline monitoring have grown in the state administration, mainly for economic reasons. The Ministry of the Environment in Finland drew up a monitoring strategy for the period until 2020 and set a target that included utilisation of new

technologies in the collection of monitoring data. On-line measurements, remote sensing and modelling are considered preferred methods [14].

According to success of the laboratories participating in PTs, the quality of analytical results produced is usually rather good and mostly the results are sufficiently comparable to each other, although the measurement uncertainty estimates may vary [15, 16, I, II]. Laboratories typically implement the quality management systems according to standard ISO/IEC 17025, which require setting up regular quality control system including validation of analytical methods and estimation of measurement uncertainties [17]. Nowadays several operators also carry out field (*in situ*) measurements of chemical parameters, but the operators usually have not estimated uncertainty for these measurements. Furthermore these measurements tend to be performed without any proper quality assurance procedures (e.g. quality control samples, participation in proficiency testing), which are commonly applied in chemical laboratories.

The anticipated pressure for utilisation of field sensors *in situ* in water monitoring requires immediate actions in setting up similar tools for assessment of the quality of data produced by these instruments. Quality assurance procedures also help the operators of these instruments to improve the quality of the measurement results.

The aim of this work is to introduce a set of new tools for enhancing quality of analytical results in water monitoring. These include tutorial computer software packages for estimation of measurement uncertainty mainly based on the approach described in Nordtest TR 537 [7] for assisting both laboratories and field sensor operators. The toolbox includes also individual examples to improve the reliability of analytical results by enhanced quality control procedures. These include an application of “in-house” reference material for DO measurement. For mercury, enriched stable ^{196}Hg isotope is applied for monitoring the stability of total mercury in water samples. A glass surface silylation procedure is applied for minimising mercury losses and contamination. Also proper organisation of proficiency tests for field sensor measurements of selected inorganic parameters is investigated. One of the tools for future water quality monitoring is based on crowdsourcing, where citizens’ observations are applied. This trend is promoted by validating an innovative measuring system for water turbidity field measurements.

4 TOOLS FOR WATER QUALITY MONITORING

In this section different practical tools for water quality monitoring are described for both laboratory and field measurements of chemical water analysis. As a summary, the tools investigated in this thesis are presented as a “toolbox” in Figure 1.

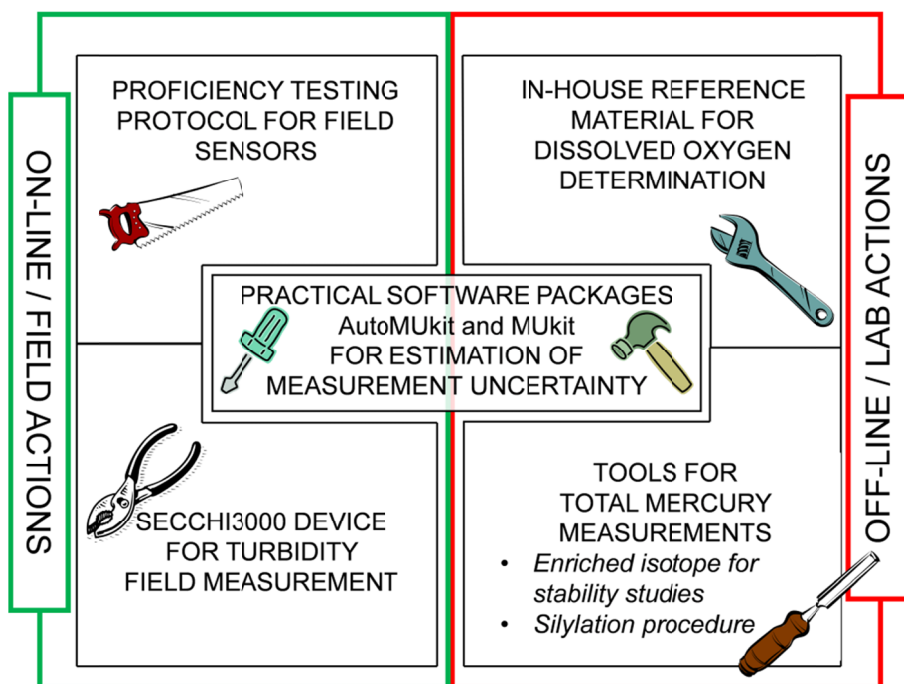


Figure 1. Tools for water quality monitoring investigated in this thesis.

4.1 Practical software for measurement uncertainty estimation

4.1.1 Background

In the last few decades, numerous guides have been published on the calculation of measurement uncertainty. Some approaches have been developed to a quite high level and have become established as valid procedures. The general principles valid for all types of measurements are described in the GUM, originally published in 1993 [4] as the Guide to the Expression of Uncertainty in Measurement and revised in 2008 [5]. Besides the general principles the GUM also describes in detail the uncertainty estimation approach based on modeling – the so called “bottom-up” approach. In this approach all relevant uncertainty contributions affecting the measurement result are estimated and combined using the model equation of the measurement. In 1995, EURACHEM and CITAC published the QUAM-guide – interpretation of the GUM for chemists – which was revised in 2000 and 2012 [6]. The GUM was created to harmonise the procedures used for measurement uncertainty evaluation. The QUAM-guide was written to help analytical chemists to use the approach described in GUM, including examples of analytical chemistry.

Since then several “top-down” approaches have been presented for measurement uncertainty evaluation. Some of them are based on inter-laboratory data [7, 18–20] whilst others are based on intra-laboratory data [7]. Silva et al. have also presented what they term the “Differential” [21, 22] or “Transversal” approach [23], where information for measurement uncertainty estimation is obtained both from the “bottom-up”, and “top-down” directions.

Eurolab have published a technical report summarising and systematising the alternative approaches to uncertainty evaluation, comparing different methods of calculation of measurement uncertainty mentioned above [8]. It emphasises that the uncertainty estimation based on mathematical modelling of the measurement procedure (modelling approach) is often (mis)conceived as being the only “GUM approach”, since it is highlighted in the GUM. In fact, alternative “empirical” approaches are also compliant with the GUM.

In 2003 Magnusson et al. published the Nordtest Technical Report – Handbook for estimation of measurement uncertainty in environmental laboratories (revised in 2004 and 2011) [7]. Its ease of use, reliance on the data available from validation and quality control has made it popular among routine laboratories. The International Organization for Standardization has recently published international standard “Water quality – Estimation of measurement uncertainty based on validation and quality control data” [9], which is essentially based on Nordtest TR 537 [7].

The Nordtest handbook [7] describes two main approaches for the estimation of combined standard uncertainty u_c . The first one, used only as preliminary uncertainty estimate, includes estimation of u_c according to reproducibility standard deviation s_R reported in a standard method from an inter-laboratory

trial [24]. The other one is the estimation of 1) the uncertainty component from within-laboratory reproducibility u_{RW} (termed as $u(R_w)$ in [7], also called intermediate precision), and 2) the uncertainty component due to possible method and laboratory bias u_{bias} (termed as $u(bias)$ in [7]). Both of these uncertainty components can be conveniently estimated from routine quality control and validation data [25], without the need for extensive dedicated experiments, thus significantly simplifying the uncertainty estimation in routine laboratories.

The Nordtest approach, using quality control and validation data, describes several different ways of estimating u_{RW} or u_{bias} (Figure 2 [II]). For u_{RW} , a laboratory can choose to use 1) the analysis results of “control sample covering whole analytical procedure” or 2) the analysis results of “control samples and routine sample replicates”. For u_{bias} , a laboratory can choose whether to use 1) analysis results of one or more “Certified Reference Materials (CRM)”, 2) the results of “proficiency tests (PT)” or 3) the results of “recovery tests” [7, I, II]. All these possible choices may result in different measurement uncertainty estimates calculated by the Nordtest approach.

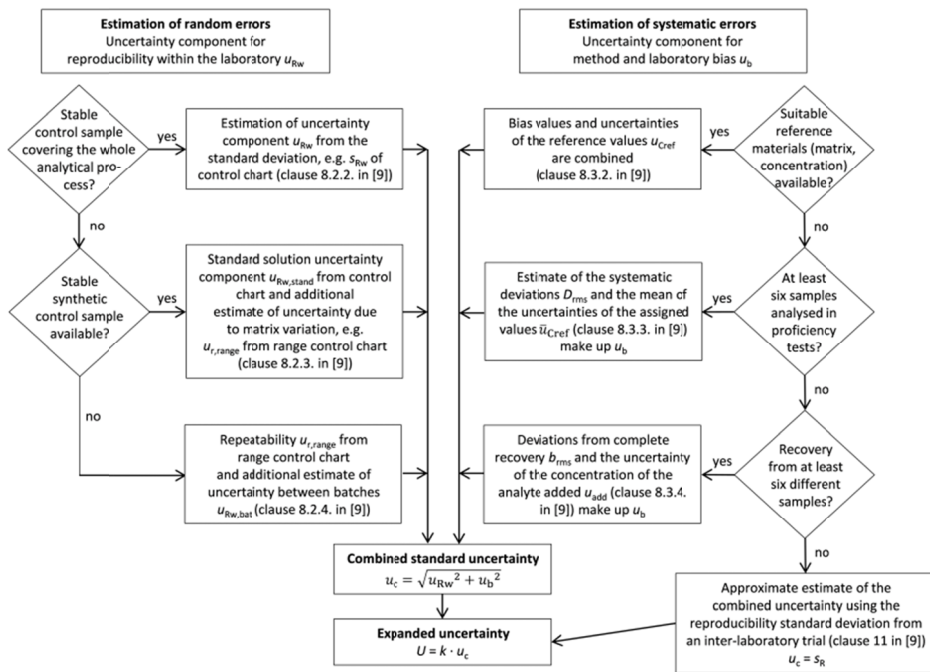


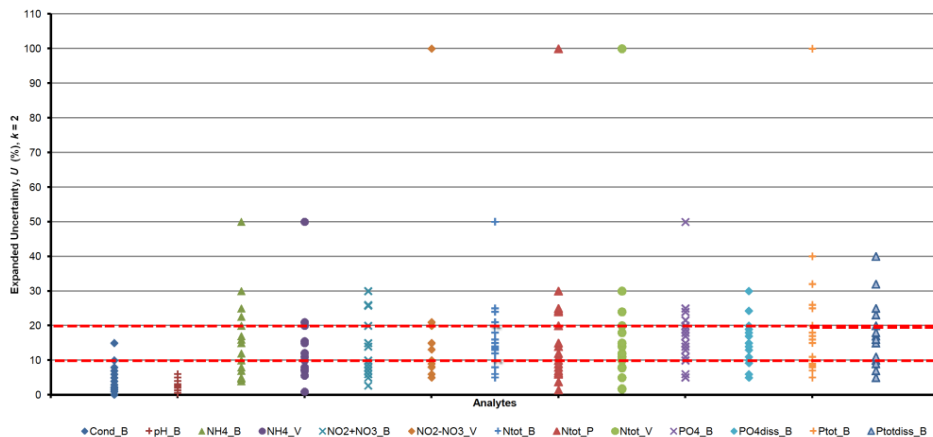
Figure 2. Schematic approach for the estimation of measurement uncertainty for one concentration level [II]. Figure is reproduced from Figure 1 in ISO 11352 [9] courtesy of ISO, Geneva.

4.1.2 The need for uncertainty estimation software

The use of applications and software assisting in the calculation of measurement uncertainty in laboratories has increased during the past decade [26, 27]. However, ten years after the initial publication of Nordtest TR 537, the approach still lacked software support. The existing software packages were based for the most part on the “bottom-up” approach. The reason for this is obviously the fact that the evaluation of measurement uncertainty, in particular using the “bottom-up” approach is remarkably difficult. The shortcoming of this approach is that it is a challenging task to perform for routine testing laboratories, and if the measurement model does not completely describe the measurement system and procedure or if some uncertainty component is neglected or underestimated, then the calculated uncertainty tends to be also underestimated.

As discovered in the recent study of Finnish proficiency test (PT) participants, laboratories reported very different measurement uncertainties for the same measurement [I]. Many reported low expanded measurement uncertainties ($k=2$) in the measurement of inorganic analytes, some of them even lower than 5% (relative) in the optimal analyte concentration range, when a realistic relative expanded measurement uncertainty would have been 10–20% when looking at the laboratories’ performance in PT. In addition, some laboratories reported their expanded measurement uncertainties being between 20 and 40% or even higher, some in the range of 50 – 100%, which can only be realistic estimates at the lower end of the measurement range. It was concluded that roughly half of the laboratories either over- or underestimated the measurement uncertainty, but underestimation was more frequent (Figure 3, [I]). Underestimation of measurement uncertainty is in fact very common, and the components missing in the uncertainty calculations have been collectively called as “dark uncertainty” [28].

The need for a software tool for measurement uncertainty estimation was asked in the survey conducted for 65 Finnish laboratories in 2011 [I]. Approximately 74 % of the respondents evaluated that they would need software for uncertainty calculations [I]. Many of the respondents answering ‘no’ to the need for the software, worked in laboratories, where none of the analytical methods were within the scope of accreditation [I]. This indicates that these laboratories may not have established a quality management system (QMS) at all, and therefore they might not estimate measurement uncertainties either, which is mandatory for those laboratories, where QMS has been established, for example according to the ISO/IEC 17025 [17].



Letters describing analytes: Cond, conductivity; NH4, ammonium nitrogen; NO2+NO3, sum of nitrite and nitrate nitrogen; Ntot, total nitrogen; PO4, phosphate phosphorus; Ptot, total phosphorus; diss, dissolved.
 Letters describing matrices: B, brackish (coastal) water; V, municipal waste water; and P, pulp&paper mill waste water.
 Dashed lines represent the expected uncertainty ranges

Figure 3. Expanded measurement uncertainties U , % ($k=2$) reported by laboratories participating in proficiency tests (for pH, conductivity and nutrient determinations) organised by SYKE Proftest in 2010 [I].

4.1.3 MUKit for laboratories

The MUKit (Measurement Uncertainty kit) software is mainly based on the Nordtest TR 537 guide [7], and it is designed mainly for routine analysis laboratories [I]. It is a wizard-like software, where the operator navigates from one window to the next (with the possibility of moving back if needed) during the measurement uncertainty estimation process, simultaneously being able to read the guidance information available. The information text refers to specific chapters of the Nordtest TR 537, where additional guidance can be found.

The MUKit software has been published as freeware with the source code included, and it is licensed under the BSD-new licence. The software is available in Finnish, English and in Russian. The software can be downloaded from the website of the Envical SYKE [29] and selected screenshots are shown in Figure 4.

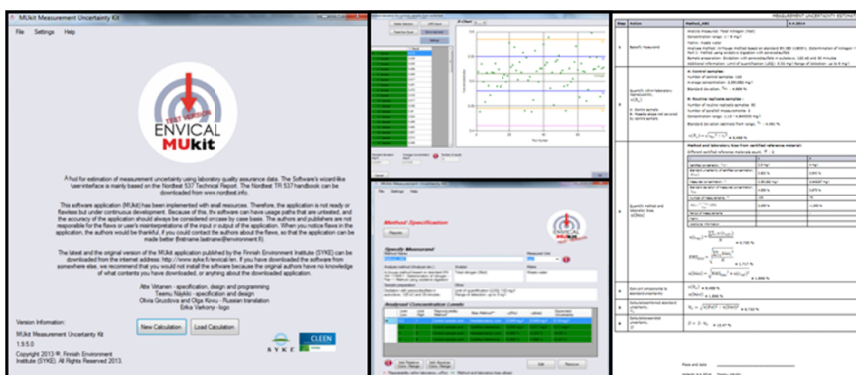


Figure 4. MUKIT software screenshots.

The calculation procedure of the software follows the guidance written in the Nordtest TR 537 [7], and the flowchart of the calculation is presented in Figure 5. The components of measurement uncertainty (u_{RW} and u_{bias}) are estimated as absolute or relative numbers. The equations used for calculating the standard uncertainties in the MUKIT software are described in detail in paper [1].

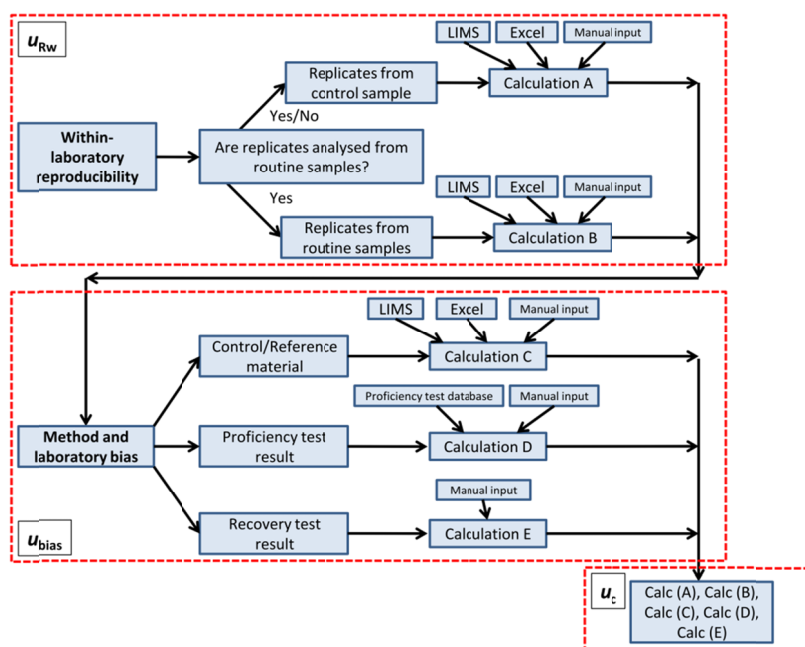


Figure 5. Flow chart of the MUKIT calculations. Measurement uncertainty estimation is based on the procedures described in the Nordtest TR 537 and is divided into two steps: estimation of within-laboratory reproducibility u_{RW} and estimation of method and laboratory bias u_{bias} . The flow chart describes also the possible sources of the initial data.

The Finnish Environment Institute SYKE, the Technical Research Institute of Sweden SP and the University of Tartu organised a study, in which the consistency of the measurement uncertainty estimations in laboratories in Finland, Sweden and Estonia was surveyed [II]. The aim of the study was to investigate the variation in uncertainty estimates when laboratories use the same set of data and the same computer software for uncertainty calculations. The data set contained hypothetical, but very realistic routine quality control and proficiency test results from testing laboratories. The laboratories were advised to use MUKIT measurement uncertainty software for their uncertainty estimations.

A total of 21 laboratories participated in the survey at the beginning of 2014, with participating laboratories in Finland ($n=16$), Estonia ($n=3$) and Sweden ($n=2$). Attention was paid to handling of the data, e.g. selecting the concentration ranges for uncertainty estimation, choosing the appropriate approach among those proposed in the Nordtest guide used for uncertainty estimation, choosing the way in which the uncertainty was reported (absolute or relative) and the outcomes of the measurement uncertainty estimations.

As a result most of the laboratories' uncertainty estimates were well within $\pm 2\%$ units from the average value in both low and high concentration ranges (Figure 6, [II]). This indicates that the unified estimation of measurement uncertainty is the way to improve the comparability of measurement results between laboratories, when their uncertainty estimates are more comparable. At the same time measurement uncertainties estimated in different laboratories are improved when the number of under- and overestimations of measurement uncertainties is reduced. This will also lead to better usability of the measurement results for decision-making processes.

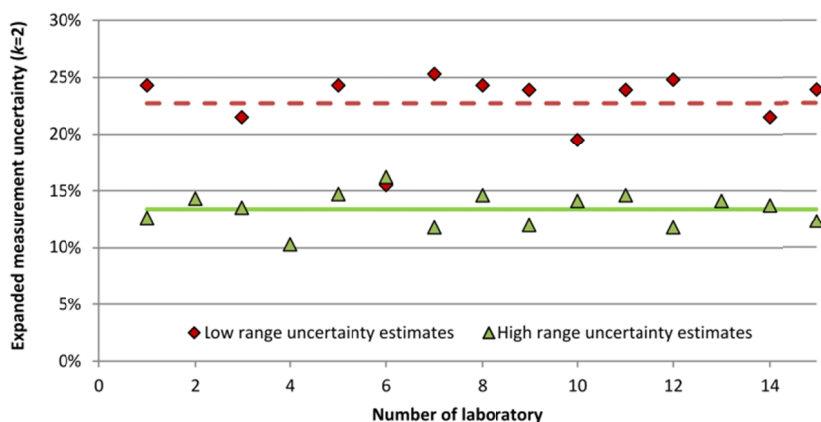


Figure 6. Relative expanded measurement uncertainty estimates calculated by laboratories for fictional total nitrogen determination in waste water. The dashed line signifies the average of the low range uncertainty estimates. The thick line describes the average of the high range uncertainty estimates. For laboratory number 6, the symbols are overlapping.

Also potential development areas in the measurement uncertainty estimation procedures were noticed [II]. Laboratories will need further understanding for the way the concentration ranges are chosen and which approach is selected for uncertainty estimation. Additionally, only few laboratories seemed to understand that for concentration levels close to the limit of quantification, the absolute measurement uncertainty should be used. According to Nordtest TR 537 [7], at low concentration levels, it is better to use an absolute uncertainty rather than a relative for most instrumental methods, as relative numbers tend to become extreme at very low concentrations (Figure 7). Though most of the laboratories studied how the random variation behaved as a function of concentration, only four laboratories estimated measurement uncertainty as absolute values in the low concentration range [II]. As the relative uncertainty increases at lower concentrations, the estimated measurement uncertainty becomes an underestimate at the limit of quantification.

Typically the decision for limit concentration between low and high range is based on the visual study of behavior of relative random variation as the function of analyte (Figure 7). Concentration range should be divided at the point, where random variation starts to increase or remains constant, respectively. An example of setting the limit concentration is shown with a dashed line in Figure 7 [II].

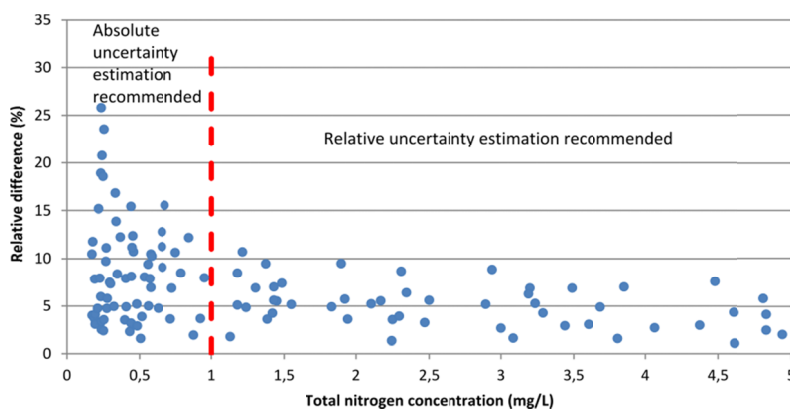


Figure 7. Study of the relative random variation as the function of total nitrogen concentration. Each dot describing random variation is calculated from the difference of routine sample duplicate results as percent from their mean value (so called r-% or R-% value [25]). Dashed line describes the limit concentration between low and high range.

In addition, many of the respondents in survey in 2011 [I] reported the use of PT results in calculating their method and laboratory bias, u_{bias} . Interestingly, this was also true for the survey in 2014 [II], where majority of the laboratories used PT results for bias estimates, although it is clearly stated in the Nordtest guide that in most cases PTs are inferior to CRMs for this purpose [7]. When

using a CRM, the bias can be determined much more reliably, using several replicates over time. Also if the PT results have been collected over a time period of several years, and the CRM results available have been analysed during the most recent year, the bias estimate based on CRM results should better reflect the laboratory's current performance. It should be also noted that uncertainty may be overestimated, if proficiency test results are used for bias estimates in the case where the random component "between laboratory standard deviation" is high and the number of participating laboratories is low. Then the uncertainty of the assigned value will become too high, leading to an overestimated bias component [II].

4.1.4 AutoMUKit for field measurements

Field sensor measurements are becoming more common for environmental monitoring. Solutions for enhancing reliability i.e. knowledge of the measurement uncertainty of the field measurements are urgently needed. Real-time estimation of measurement uncertainty for field measurement has not been previously published and in paper [III] a novel approach for the automated turbidity measuring system with a computer software application for real-time uncertainty estimation based on Nordtest handbook's [7] measurement uncertainty estimation principles is outlined.

There are two main requirements for the estimation of real-time measurement uncertainty of an on-line field turbidity measurement 1) setting up automated turbidity measuring system that can be (preferably remotely) controlled. System measures turbidity of the samples (water to be investigated as well as synthetic turbidity control samples) the way the user has programmed it and stores the results in a database. 2) Setting up automated data processing (software) where the measurement uncertainty is calculated from the data produced by automated turbidity measuring system. The software is not restricted to turbidity measurements, but will enable measurement uncertainty estimations for any kind of automated measuring system that perform sequential measurements of routine samples and control samples/reference materials similarly as described in paper [III].

For applying real-time estimation of measurement uncertainty, an automated turbidity measuring system was constructed, and it operated by taking water samples via tubing into the instrument's flow-through cell [III]. Using the valves, it was possible to automatically introduce natural water samples, as well as, turbidity standard solutions to the turbidity detector (Fig. 8).

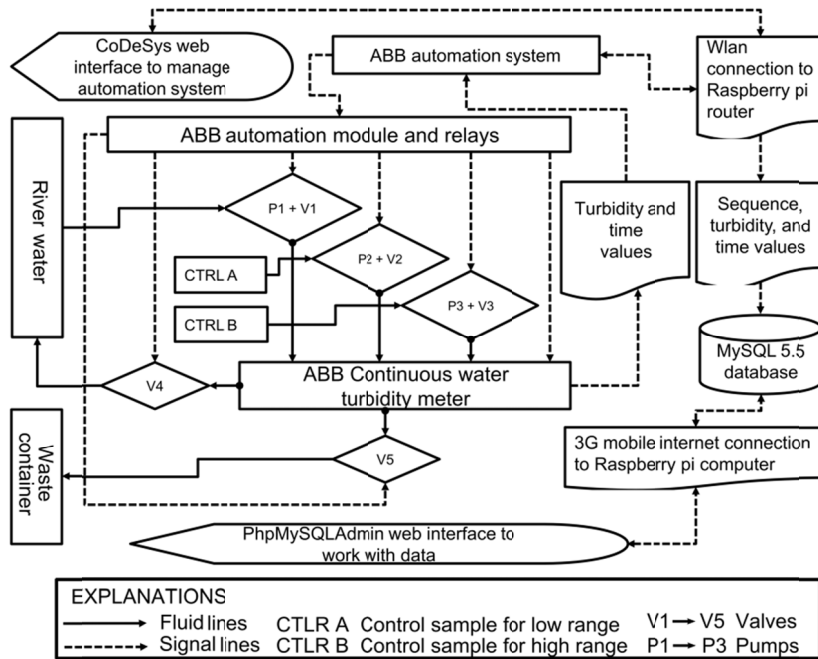


Figure 8. Automated turbidity measurement system, which sequentially measures river samples and two control samples (CTRL A and CTRL B) and reports the data to a database [III]

A software application (AutoMUKit) was programmed for carrying out real-time measurement uncertainty estimation [III]. For the measurement uncertainty estimation, the information on random and systematic errors of the measurement is needed (Fig. 2), as described in Nordtest TR 537 [7] and ISO 11352 [9]. The information is obtained by replicate measurements of the water to be investigated as well as synthetic turbidity control samples.

Automated measuring system is required to produce the database file (csv, comma-separated values) in the following form:

```

...
A,2014-05-14 15:00:00,3.523
A,2014-05-14 15:00:05,3.545
A,2014-05-14 15:00:10,3.530
D,2014-05-14 15:00:15,0.000
A,2014-05-14 16:00:00,3.427
A,2014-05-14 16:00:05,3.455
A,2014-05-14 16:00:10,3.441
D,2014-05-14 16:00:15,0.000
B,2014-05-14 16:30:00,3.987
B,2014-05-14 16:30:05,3.976
B,2014-05-14 16:30:10,3.969
...

```

where the comma separated columns are:

1. Type of the sample
A = Routine sample
B = Control sample for low concentration range
C = Control sample for high concentration range (type of the sample not shown in the example data)
D = A marker sequence showing that a replicate series of routine sample measurements has finished
2. Date in the form of YYYY-MM-dd HH:mm:ss (Y = year, M = month, d = day, H = hour, m = minute, s = second)
3. Measurement result with a dot as the decimal separator.

A row defines a measurement result. The rows are separated with a new line.

Figure 9 shows the raw measurement data consisting of one measurement result in one row with information about the sample type, the measurement date and time. Three parallel turbidity measurements are carried out within a five seconds interval from routine (river water) sample “A”. After 60 min, another three replicates are measured. Later in the sequence there are measurement results for synthetic control sample “B” with a turbidity value in the low concentration range.

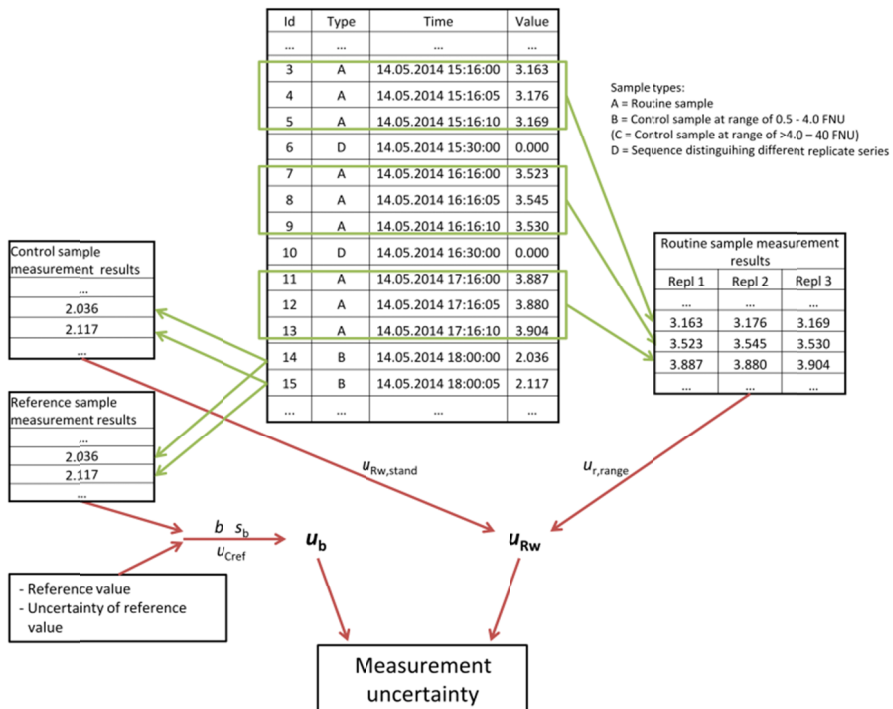
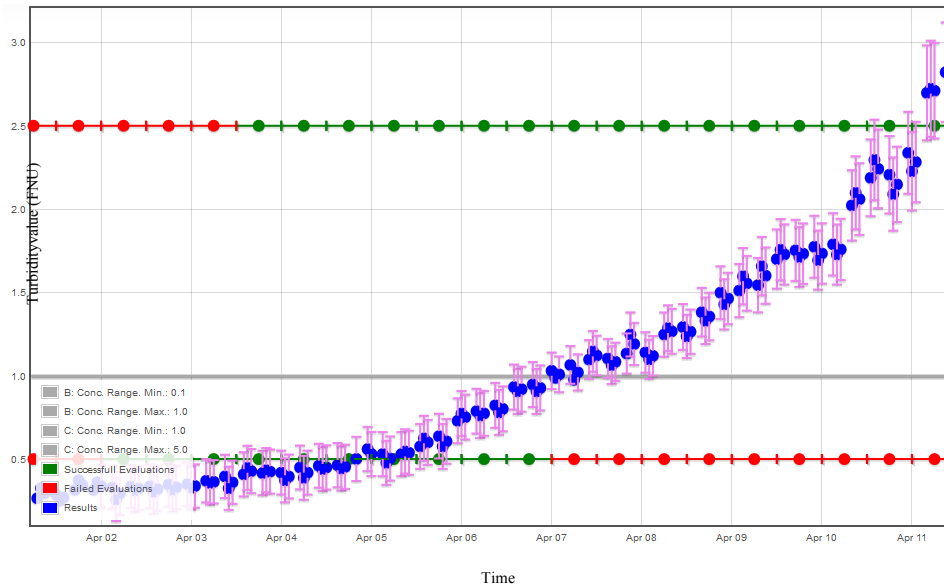


Figure 9. The general functioning of the real-time uncertainty estimation [III]

According to given parameters, the AutoMUKit software application performs queries for the measurement results and the measurement uncertainty is calculated. Parameters described in paper [III] can be adjusted and their influence on the measurement uncertainty can be assessed visually using the visualisation tool developed. The graphs include e.g. the presentation of measurement results and their uncertainties ($k = 2$) shown using error bars (Figure 10), X-chart for visual monitoring of the measurement results of control samples, and r% chart for monitoring the random variation as a function of the measurand value or concentration [25, III].



B Conc. Range Min./Max. shows the minimum and maximum concentrations for control sample B (=low concentration level).
C Conc. Range Min./Max. shows the minimum and maximum concentrations for control sample C (=high concentration level).

Figure 10. Measurement results with their uncertainties ($k = 2$) versus time for an on-line turbidity measuring system [III]

The benefits of advanced utilisation of field measurements are enormous. The measurement results are produced in very high frequency and the use of the equipment do not require manual operation, except when maintenance is needed. The alteration of the sample during the transportation to the laboratory and storage is not relevant in the field measurement. Sensor measurement results may occasionally drift for many reasons e.g. due to bio fouling, but this can be well monitored using the approach presented in the paper [III]. When control samples with a known value or concentration is measured regularly, also information from changes in calibration can be detected. Additional benefit is that the occurred drift can be taken into account (in real-time) as bias value in the measurement uncertainty calculation or the measurement results of the

control samples can be used for real-time recalibration of the measuring device. The measurement results will become more useful as they are associated with the uncertainty information. They can be compared to the measurement results produced in laboratory and they can be more easily used for decision making processes.

4.2 Protocol for field sensors' proficiency testing

Laboratories typically implement the quality management systems according to standard ISO/IEC 17025, which require setting up regular quality control system including validation of analytical methods and estimation of measurement uncertainties [17]. The laboratories demonstrate their performance for example in PTs. The anticipated pressure for utilisation of field sensors *in situ* in water monitoring requires immediate actions in setting up similar tools for assessment of the quality of data produced by these instruments. Quality assurance procedures also help the operators of these instruments to improve the quality of the measurement results. One important tool for assuring the quality is participation in proficiency tests (PTs). The results from PTs provide knowledge about the comparability of measurement results, which is important both to the operators as well as to the end user.

In situ PTs are intercomparison measurements, where all the participants (with their own equipment and using their own competence) measure the same sample continuously at the same time, at the same site [30]. This arrangement provides the best possibility for assessing participant performance (Participant = laboratory participating in the intercomparison and sending a worker and an instrument to the intercomparison).

In situ intercomparison measurement of dissolved oxygen concentration was organised at laboratory facilities in 2012 at the University of Tartu, Estonia [31, IV]. In 2013, Proftest SYKE organised the first such a PT in Finland for field measurements of temperature, conductivity, dissolved oxygen concentration, oxygen saturation, and pH-value in natural water [32]. In total, 9 participants and 16 sensors took part in this proficiency test. The protocol of the field PT is presented below and in paper [V].

4.2.1 Selection of the site

The site was selected in Southern Finland near the capital area since this way organising PT was easier to carry out and the possibility to have enough participants was higher. The place selected was near the centre of Vantaa city, where the river Kerava flows through. The place was easy to arrive i.e. there were large parking areas near the PT site and good public transportation connections were available for participants and there was enough space for carrying out the measurements. Appearance of the river water is naturally turbid, since most of the water flows through clayey arable areas [V].

At first the purpose was to utilise for the test area the bridge, which crosses the river, but that was too high for participants having sensor with cable less than 5 meters. Next to the bridge on the shore there was a pier, where the sensors could be easily mounted (Figure11). The river flow was uniform enough around the pier and especially where the sensors were located [V].



Figure 11. The PT Site. The metal rod was used for mounting the sensors to the pier and selected test depth [V].

4.2.2 Protocol for homogeneity studies and PT measurements

The homogeneity and temporal stability of the river water at the PT site was studied by measuring pH, conductivity and dissolved oxygen with three similar YSI 600 XLM V2 sensors. These sensors were placed in both of the ends and in the middle of the pier at three different depths for obtaining information on spatial heterogeneity (A, J and P in Figure 12). This preliminary homogeneity study was carried out two hours before starting the PT to ensure that the test site was appropriate. During the PT, all homogeneity test measurements were carried out at depth of 70 cm starting at time 11:15 and ending at 11:30. Actual comparison test measurements were carried out at 11:22 and 11:27 [V].

For homogeneity test, ten results (H1 – H10) were recorded during about timeframe of three minutes (1.5 min before and 1.5 min after the actual comparison test). Sensors recorded values measured from water body every two seconds. Two consecutive measurements were regarded as replicate measurements for one homogeneity test sample (Figure13, [V]).

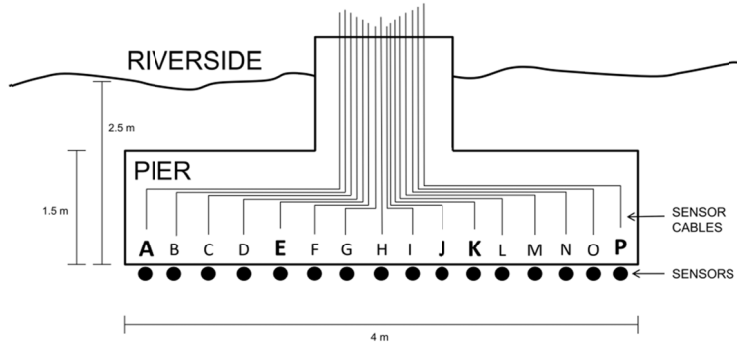


Figure 12. A top view of installation of the sensors on the pier. Sensors A, E, J, K and P were used by PT provider [V].

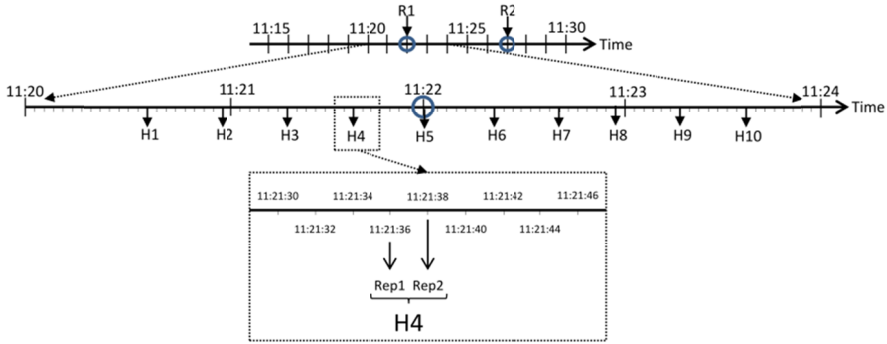


Figure 13. Time frame for the homogeneity testing. Homogeneity test samples are indicated as H1...H10. Rep1 and Rep2 are two replicate measurements of one homogeneity test sample. Actual PT samples were measured at 11:22 (R1) and 11:27 (R2), marked with circles on the Time-axis [V].

To assess homogeneity of the samples, both spatial and between measurement time variability standard deviations during the test were obtained using variance component analysis [V].

As the PT was dealing with *in situ* measurements from naturally flowing water, the sources of uncertainty were not as easily controlled as in laboratory environment. By conducting the homogeneity testing simultaneously with the actual PT experiments, it was tried to ensure that the measured water was sufficiently homogeneous for all the participants.

For statistical analysis of uncertainty components, independent sources of variation were assumed and the total variation was divided in three parts: time of the measurement (temporal heterogeneity), spatial heterogeneity of the test area, and analytical precision as described in eq 1 [V].

$$\sigma_{\text{total}}^2 = \sigma_{\text{time}}^2 + \sigma_{\text{samp}}^2 + \sigma_{\text{anal}}^2 \quad (1)$$

where

σ_{total}^2 = total variation of the homogeneity test dataset

σ_{time}^2 = variation due to temporal heterogeneity

σ_{samp}^2 = variation due to heterogeneity of the test area (sampling)

σ_{anal}^2 = variation due to analytical precision

Estimates of the variance components were obtained by analysis of variance (ANOVA) procedure in accordance with Eurachem guidance [33].

Processing of the data, setting the assigned values and assessing the performance of the different sensors are described in paper [V].

4.2.3 PT results

The standard deviation of the participants' results for the PT organised by Profest SYKE was lower than the organiser expected. Actually for assessing the performance of the participants, the same values were used for the target standard deviation for performance assessment than in proficiency tests organised for chemical laboratories during the past few years. In this proficiency test, 80 % of the results for pH, 79 % for conductivity, but only 69 % for dissolved oxygen concentration results were regarded as satisfactory [V].

The participants using DO sensors with the optical measuring principle performed better than participants using amperometric sensors. The reason for this may have been the fact that optical sensors are more robust in routine use and more stable in time than amperometric sensors. The latter need more maintenance (replacement of the membrane and electrolyte solution), more frequent calibration and they are more sensitive to stirring of the solution and temperature [34].

Similar findings were obtained in the intercomparison carried out for DO measurements in 2012 at University of Tartu [IV]. Out of altogether 63 DO measurement results obtained by the participants, 52% were unacceptable according to the E_n numbers. Participants using optical sensors performed better than participants using amperometric sensors.

Both intercomparisons [IV, V] revealed that most participants had not estimated measurement uncertainties for their sensor measurement results [IV, V], even though some of them were accredited according to the ISO/IEC 17025 [17]. DO concentration is a highly unstable parameter of water. Thus the preparation of reference solutions that are stable for extended periods of time is impossible. This complicates the standardization of the measurements and rules out preparation of CRMs. A way to promote measurement uncertainty estimations for the DO concentration measurement results is to use a tool presented in paper [IV]: “in-house” reference material – water saturated with air. The reference material together with routine sample replicate results and

control charts (X-chart and R-chart) enables operators of the sensors as well as the Winkler titration systems to estimate measurement uncertainty of the DO concentration measurement results with the Nordtest approach [7] more easily and more reliably than before.

For maintaining the control charts [25], ideally a data point should be recorded every day on which the measurements are performed. This enables observing trends and taking actions before things get out of hand [IV]. In addition setting up control charts and participating in interlaboratory comparison tests may be exploited to check, if the self-declared uncertainty estimate is realistic [35].

Quality assurance data of the results of sensors are also necessary to be collected before sensors can be used on a larger scale in national environmental monitoring programmes. Also knowledge about the expanded measurement uncertainties has a key position for the usefulness of the results. Estimation of the measurement uncertainty will also give user information on sources of random variation and bias of the method, which is highly important during the method development [V].

Performance-based requirements allow using methods that are validated and proved to produce reliable measurement results for particular case [13, 14]. This approach will enable also the use of field and on-line measurements for monitoring purposes. SYKE has recently published quality recommendations for laboratories producing and delivering environmental monitoring data to water quality registers in Finland [36]. The recommendations include the accreditation of the methods as well as minimum criteria for limits of quantification and measurement uncertainties.

According to the results of PT organised by SYKE [V], some of the participants performed well and after they have successfully validated, and preferably accredited or certified, their methods as well as established internal and external quality assurance protocols (X-charts, R-charts, proficiency test schemes etc.), these participants could produce information for water quality monitoring purposes [V].

4.3 Crowdsourcing in water quality monitoring

Water resources management carried out under the European Union's (EU) water policy and national legislation on water resource management require knowledge of the chemical and ecological state of waters and measures for achieving good water status [10, 11]. Turbidity is an essential parameter for describing water quality by direct and indirect impacts on fish, invertebrates and aquatic plants. Turbidity determinations are carried out extensively in Finnish surface waters. In 2012 total of over 30 000 turbidity measurements were performed mostly in Finnish lake, pond, river, and brackish waters.

Currently, environmental monitoring measurements are carried out with appropriate quality by accredited testing laboratories, but there are pressures to streamline monitoring, and a need for employing the third sector i.e. citizens and voluntaries in environmental monitoring. The Ministry of Environment in Finland drew up a monitoring strategy for the period up to 2020 and set a target that included the utilisation of new technologies in the collection of monitoring data. While on-line measurements, remote sensing and modelling are considered the preferred methods, the role of citizen-based monitoring should also be expanded [14].

A device called "Secchi3000" was developed at SYKE as a low-cost and simple-to-operate tool so that water quality measurements can also be carried out by non-experts and citizens [37]. The Secchi3000 measuring system is composed of three parts (Figure 14):

1. **Device.** This includes a plastic container that has one side transparent for light, a measurement structure that goes into the container, and a lid with a hole. The measurement structure has white, black and grey target areas at two depths (10 cm vertical distances between the target areas). The user fills the container with water from a lake, river or sea and places the measurement structure in the container.
2. **Mobile phone with a measurement application (MA).** The software installed on the phone controls the camera and allows the user to take a measurement photograph and input other observations. The software sends the photograph with other information (e.g. GPS position) to the server.
3. **Server.** The server receives and analyses the measurement photographs automatically with an algorithm, which finds the target areas from the picture and computes parameters of water quality. Finally, the results are sent back to the user's mobile phone and stored in a database.

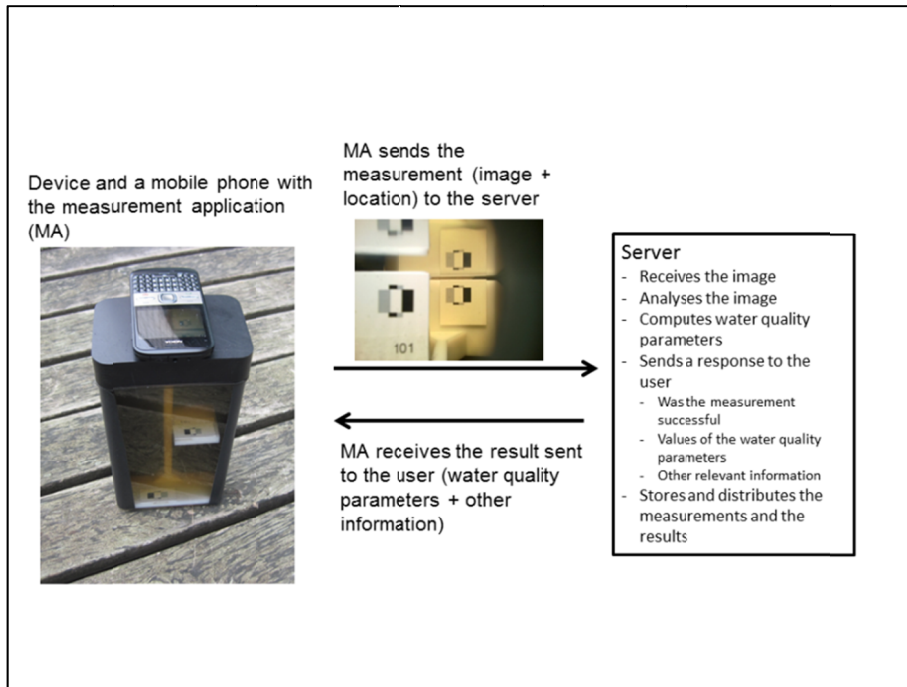


Figure 14. Secchi3000 measuring system.

The Secchi3000 measurement principle is based on the comparison of intensities of light measured over black, white and grey target areas at two depths. The basic assumption is that the target areas at both depths have the same downwelling irradiance at the surface. This is achieved by placing the transparent side of the container towards the sun or the brightest part of the sky. Thus, the differences in the apparent brightness of the target areas when viewed from above are caused by the optical properties (scattering and absorption by particles and dissolved substances) of the water column between the target levels. By using the black and white targets it is possible to measure the attenuation caused by water. The grey targets are used for reducing the effects of the difference of exposure properties of different cameras or illumination conditions (sunny or cloudy).

Since digital cameras give values for three wavelength ranges (corresponding to red, green, blue light), it is possible to measure the attenuation in these three wavelength regions. Using empirical equations, it is possible to calculate from the attenuation values different physical or chemical parameters describing the water quality. The equation for turbidity measurement has been calibrated using results obtained with laboratory measurements. Laboratory measurement of turbidity is based on scattering of light. The set-up of the device and the detection of target positions of white, grey and black areas are described in more detail in [37].

Secchi3000 was validated for turbidity measurements in Finnish natural waters (river, lake, pond and brackish waters) (Figure 15, [VI]). Validation included an estimation of the limit of quantification, investigations of the influence of water colour and illumination conditions on turbidity values, and the estimation of measurement uncertainty. A comparison of turbidity results obtained with the Secchi3000 and HACH 2100AN IS laboratory instrument in natural water samples and turbidity reference samples was carried out. In addition, turbidity values obtained with different mobile phones were compared. The tests are described in more detail in paper [VI].



Figure 15.Testing of Secchi3000 measuring system.

According to the results of validation, Secchi3000 measuring system was appropriate for the measurement of turbidity lower than 7 FNU [VI]. The algorithm applied for the current turbidity calculations is not fully suitable for higher turbidities. For potential routine use this is not a major problem, since turbidities in Finnish natural waters are usually low. In May-September 2012, an average of 89 % of the measured surface water turbidity values were below 7 FNU in Finnish lake waters ($n=2770$) and 57 % in rivers ($n=4787$).

Another problem is that approximately 40 % of the results in lake waters and 20 % in river waters were even below the LOQ (1.7 FNU) of the Secchi3000. Therefore, further development of the Secchi3000 is needed, particularly for achieving a lower limit of quantification. One potential method for this is to increase the path length of the device. With a longer path length the attenuation will increase and samples with lower turbidities can cause enough attenuation for the measurement [VI].

The achieved expanded measurement uncertainties (at $k=2$ level) may be underestimated due to the low amount of data used in calculations. When routine laboratories estimate the measurement uncertainty based on a quality control data, to achieve a representative basis for the uncertainty calculations and to reflect any such variation, the number of results should ideally be more

than 50 and cover a time period of approximately one year, but the need differs from method to method [7]. For measurement of turbidity with the Secchi3000, probably 50 – 100 measurement results covering a time period of approximately one summer (four months) would give more reliable uncertainty estimates. During the validation tests the amount of data available is usually restricted. In this validation study, the number of tests was lower and the time scale was much shorter. The measurement uncertainty needs to be re-estimated with more comprehensive data.

According to quality recommendations for producing environmental monitoring data in Finland, the LOQ for water turbidity measurement is 0.5 FNU, while the recommendation for expanded measurement uncertainty ($k=2$) is 0.2 FNU for the range of 0.5–1.0 FNU and 20 % for the range of >1 FNU[36]. The present estimate of measurement uncertainty for the Secchi3000 is higher than in the recommended quality criteria for official monitoring methods at turbidity values below 3.5 FNU. With higher turbidities (up to 7.0 FNU), the quality criterion for expanded measurement uncertainty is fulfilled. For official monitoring purposes, the LOQ needs to be less than one third of what is presently achieved.

As the global trend is from standard-based towards performance-based requirements, new innovations such as Secchi3000 may also achieve the status of an officially approved monitoring method. Before achieving this status, the device has to prove it is able to produce reliable measurement results, particularly to fulfill the set quality criteria for measurement uncertainty and limit of quantification. The method should preferably be accredited or certified, as well as having established internal and external quality assurance protocols, before producing official information for water quality monitoring purposes. Therefore the next goal is to lower the limit of quantification and measurement uncertainty.

Although the present configuration of the Secchi3000 device is not yet fully suitable for official monitoring, it will already enable the involvement of the third sector in the monitoring of water quality and this way citizens' observations could serve at least as supplementary information for reporting and surveys, which was actually the original purpose of the Secchi3000 from the beginning.

4.4 Stability study procedure for trace element determination

Stability of the sample during transportation and storage is essential for trueness of the measurement result. Preservation of samples without any alterations, whether wastewater, industrial wastes, or natural waters, is practically impossible, because it is never possible to achieve complete stability of every constituent [38]. Most preservation techniques only retard chemical and biological changes that inevitably continue after sample collection. Several processes may

occur in the sample during the storage time [38]. These include e.g. oxidation, reduction, absorption, adsorption and volatilisation. Preservation methods are limited to pH control, chemical addition, the use of amber and opaque bottles, refrigeration, filtration, and freezing[38]. Trace elements are usually stable in the sample for several weeks, if the samples are preserved with an acid to pH <2 and stored in a refrigerator.

Stability of total mercury in water samples was selected under investigation in this work, due to mercury's highly toxic nature in the water environment and its' importance in environmental monitoring programmes. Member states in the EU are obliged to monitor concentration of mercury and its compounds in water environment according to the Water Framework Directive (2000/60/EC) [10] and in particular the Priority Substances Directive [39], which set Environmental Quality Standards (EQS) for the substances in e.g. surface waters (river, lake, transitional and coastal) and confirmed their designation as priority or priority hazardous substances.

Another reason for selecting mercury for stability studies was the fact that routine testing laboratories use several guides and standards for the measurement of total mercury in water samples. These standards give different recommendations for storage times of water samples intended for total mercury analysis. [38, 40–44]

The standard EN ISO 17852 [40] suggests to preserve samples preferably on site using hydrochloric acid, potassium bromide and potassium bromate reagents. EN ISO 17852 suggests carrying out total mercury analysis within seven days after collection. According to the EPA method 1631 [41] the samples for total mercury analysis should be either preserved or analysed within 48 h of collection. EPA 1631 suggests preserving samples with BrCl reagent containing hydrochloric acid, potassium bromide and potassium bromate. According to the EPA method, after preservation the samples are stable for up to 90 d of the date of collection.

From other standards, ISO 12846 [42] suggests to analyse total mercury within 2 weeks. Standard methods for the examination of water and waste water [38] gives 28 days as maximum storage time whereas ASTM standard D3223 - 12 [43] gives 38 days respectively. Standard ISO 5667-3 [44] presents the maximum storage time to be as long as 6 months using preservation with HNO₃ to pH in the range of 1 to 2.

A novel tool for investigation of stability of total mercury in water samples using enriched ¹⁹⁶Hg stable isotopic reagent is proposed in this work. Natural abundance of ¹⁹⁶Hg in water samples is 0.15%. Thus adding accurately known amount of enriched ¹⁹⁶Hg isotope to the samples, reliable information on alteration of total mercury mass concentration can be obtained [VII].

4.4.1 Setting the reference value

The mass concentration of ^{196}Hg in the non-spiked sample in the beginning of the stability study (time=0 (t_0); $c_{\text{OR0}}(^{196}\text{Hg})$) was unknown and had to be found. As can be seen from Figure 16, at time t_0 added (weighed) amount of ^{196}Hg was known. At time = 1 (t_1), ^{196}Hg was analysed in the spiked sample and ^{202}Hg was analysed in non-spiked sample. Mass concentration of ^{196}Hg in the non-spiked sample at time t_0 is calculated from the measurement result of ^{202}Hg in non-spiked sample at time t_1 , as presented in detail in paper [VII].

The total mass concentration of ^{196}Hg in the non-spiked sample at time t_0 is formed from the known mass concentration of spiked ^{196}Hg , and by experimentally calculated mass concentration of ^{196}Hg in the original non-spiked sample (nearly 0%). This total mass concentration of ^{196}Hg at time t_0 represented the “reference value” for the other total mercury measurement results obtained at the stability study period [VII].

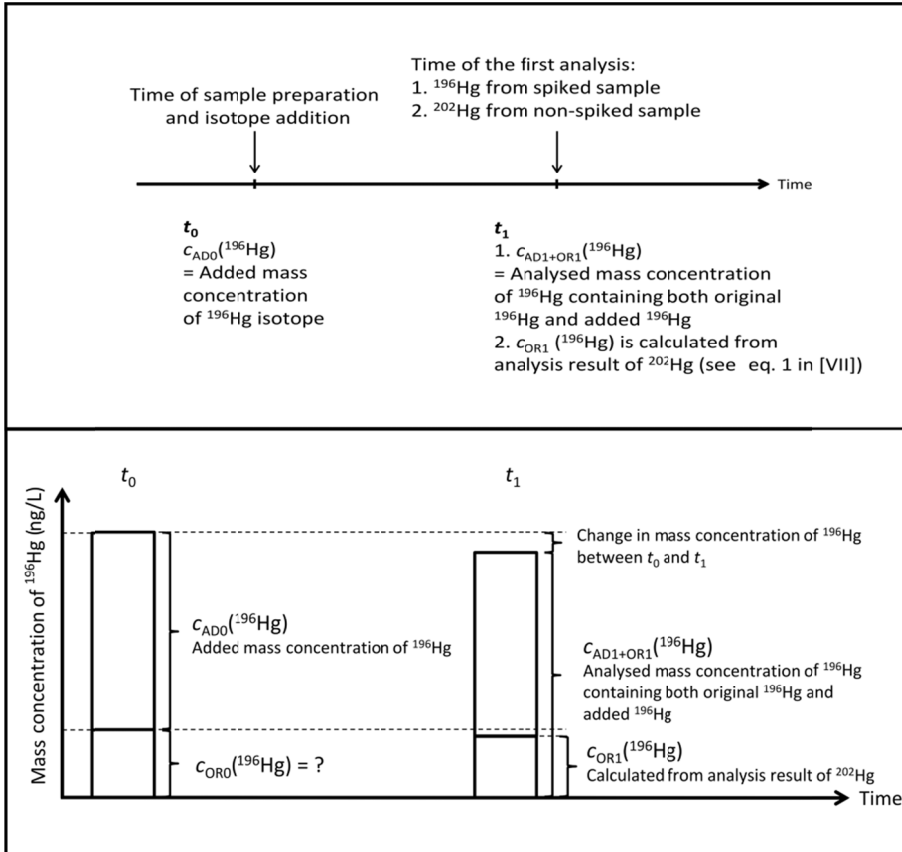


Figure 16. Calculation of the unknown mass concentration of ^{196}Hg in the non-spiked sample in the beginning of the stability study ($c_{\text{OR0}}(^{196}\text{Hg})$; t_0).

4.4.2 Stability studies

Three different sample types were tested according predefined study protocol and for approximately three month time period [VII]. Two of the tested sample types were proficiency test (PT) samples and the aim was to find out for how long time the SYKE proficiency test provider can store the PT samples after their preparation. As usually, the PT samples were collected several months before homogenisation and dividing the water into the bottles. PT sample matrices were natural river water (total Hg concentration ca. 150 ng/L) and industrial waste water (total Hg concentration ca. 2000 ng/L). In addition to PT samples, also natural water with near-background total Hg concentration (ca. 10 ng/L) was tested. Mercury concentration was measured with cold vapor ICP-MS procedure [VII].

In estimation of stability of total mercury in water sample, the ASTM standard D4841 was applied [45]. D4841 demonstrates the estimation of the “holding time” (storage time) by means of replicate analyses at discrete time intervals using a large volume of a water sample that has been properly collected and preserved. Concentration of the constituent of interest is plotted versus time. The maximum storage time is the period of time from the sample collection to such time that degradation of constituent of interest or change in the sample matrix occurs and the systematic error exceeds the confidence interval of the test calculated around the mean concentration [45].

The standard D4841 suggests calculating the range of tolerable variation (d ; 99 % confidence interval) according to eq. 2.

$$d = \pm \frac{t \cdot s}{\sqrt{n}} \quad (2)$$

where

d = Range of tolerable variation from the “reference value” (ng/L)

t = Student’s t -value for a two-tailed 99 % confidence interval ($t = 3.00$)

s = Standard deviation of 10 parallel samples (ng/L), and

n = Number of replicate measurements used at each time interval in the storage time determination.

The standard deviation in eq. 2 suggested by the standard D4841 has in this study been replaced by standard uncertainty (u_c) of the measurement in the corresponding concentration range [VII]. This was chosen due to the fact that analysing parallel samples during one day, the typical day-to-day variation will not be included in the standard deviation. The standard uncertainty was calculated from the expanded measurement uncertainty by dividing it with the coverage factor ($k = 2$). The expanded uncertainty (U , $k = 2$) for total mercury measurement in natural water is 10 % and for waste water 15 % respectively at the mass concentrations studied [VII].

The tolerable range of variation (95 % confidence interval) from the initial mean concentration that was used as the criterion for the storage time evaluation was calculated as follows [VII]:

$$d = \pm k \cdot u_c \quad (3)$$

where

k = Coverage factor at 95 % confidence interval ($k = 2$ was used), and
 u_c = Standard uncertainty of the measurement (ng/L)

Division by the factor of \sqrt{n} , as suggested in eq. 2, was not necessary, since u_c has been calculated taking into account that replicate measurements were performed. This way the division by \sqrt{n} is included already in u_c itself. If u_c would be to a significant part due to systematic effects then dividing by \sqrt{n} would lead to too optimistic d [VII].

Experiments showed that the enriched ^{196}Hg isotope can be applied for the stability study successfully. Previously the proficiency test samples for total mercury measurement were advised to be analysed within 14 days. In this study the samples were stable for more than three months, if they were stored at temperature of 4–6 °C (Figure 17) [VII]. The results of this stability study were in line with the guidance presented in EPA standard 1631 [41]. However, the samples were proved to be stable for much longer time than is presented in the standard method ISO 17852 [40].

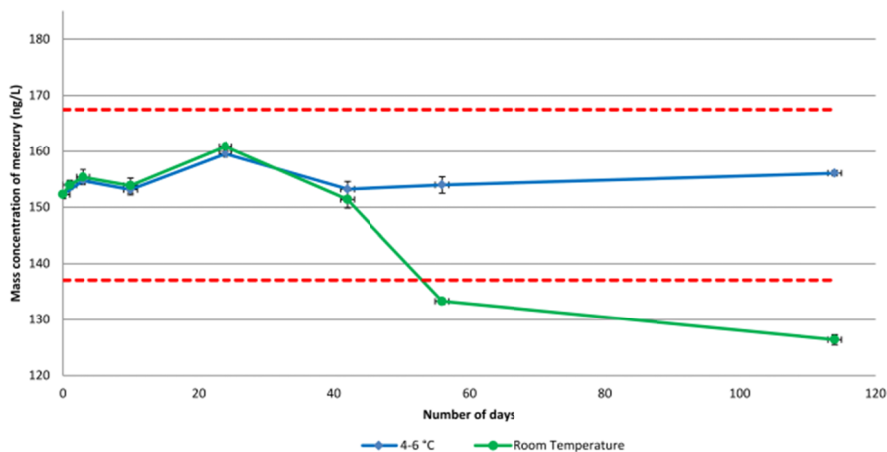


Figure 17. Storage time determination for natural water with two different storage temperatures. Initial ^{196}Hg mass concentration was ca. 150 ng/L. Dashed lines represent the range of tolerable variation. Each plot describes average of four replicates with their standard deviation.

The stable nature of ^{196}Hg is a benefit as there is no risk of radioactivity. The drawback is the poor availability and the high price of ^{196}Hg isotope materials. Although just few milligrams of ^{196}Hg isotope reagent is enough for spiking of several thousands of samples for stability studies. The preparation of the samples for this stability study was rather easy, but required careful planning in advance. In this study, particularly for natural water sample with low mercury concentration, the ^{196}Hg isotope was added only after about 20 hours after sampling, so there is no exact information on how much the Hg mass concentration had changed between the time of sampling and the time of isotope addition. However, the sample was preserved with hydrochloric acid already in the field, which decreases the probability of the total concentration significantly changing between the times of sampling and isotope addition [VII].

The natural abundance of ^{196}Hg isotope is only 0.15%. As a result the background signal of the ^{196}Hg isotope is very low in typical natural waters, even if there is mercury present. The background signal can be ignored provided a sufficiently high spike of enriched ^{196}Hg is used. This is an advantage since it can be assumed that all the measured ^{196}Hg originates from the spike added by the analyst, and therefore any changes in mass concentration are easily monitored and assessed. If the ^{202}Hg isotope (or any other common mercury isotope) would be used as a spike, then the problem would always be the accurate assessment of the reference value, since the original ^{202}Hg mass concentration could not be ignored. Due to the low background, the use of enriched ^{196}Hg instead of a more abundant natural isotope enables a much lower mass concentration of the spike, which is within the mercury mass concentration range present in natural waters [VII].

The stability study procedure would be improved, if the enriched ^{196}Hg spike could be added to the fresh natural water faster than in this study. It would be improved even more, if the spike could be added to the water sample already in the field at the time of sampling. This would require the gravimetric preparation of some kind of a pill or capsule containing exactly known mass of ^{196}Hg isotopic material as well as the preservation acid. This kind of “quality assurance pill” could also be useful in other measurements, where samples have long transportation and storage times or where the environmental conditions (light, temperature) are not optimal for sample storage [VII].

Another improvement to the procedure presented could also be the application of an isotope dilution method for mercury analysis [46–48]. This is known to improve the accuracy (trueness and precision) of the analysis, which would lead to decreased day-to-day variation and therefore more reliable threshold values for storage time study and more reliable observations of out of range situations.

The stability of mercury solutions is affected by many factors. Therefore the major interest in the future would be applying this stability study procedure for different types of waters taking into account factors such as temperature, seasonal variation (winter/summer), sample vessel material and/or sample pretreatment (e.g. filtration).

4.5 Silylation procedure for minimising the interference effects caused by mercury losses and contamination

Leermakers et al. [49] presented two mechanisms, which are responsible for the loss of mercury from solution. These are volatilisation of the analyte and its' adsorption on the container surface. Hg^{2+} can be reduced to Hg^{1+} in the presence of a reducing agent occurring either naturally (i.e. micro-organisms, humic acids) or as an impurity in solution. Hg^{1+} will then disproportionate spontaneously producing volatile mercury Hg^0 , which escape from the solution. Many problems are also encountered with PE bottles. Active sites on the interior wall surface (such as hydrocarbon radicals and carbonyl groups) and additives (amino, thiol, sulfide of phenolic groups) can cause mercury loss by adsorption and reduction. Adsorbed mercury is also very hard to remove from contaminated surfaces [49].

Therefore, low pH value, high ionic strength, and oxidising or complexing environment will help keeping mercury in solution. Low pH and high ionic strength prevents adsorption on the container walls, while oxidising and complexing agents keep the inorganic mercury as Hg^{2+} [49]. Pyrex® glass bottles or containers made of PTFE or FEP have been found to be suitable materials for the storage and measurement of mercury solutions, superior to PE [49].

The silylation technique has been applied for treating the surfaces of the injector lines in gas chromatography [50]. With the silylation reagent the free silanol groups of the glassware are able to form an inert surface. There are a number of excellent references on silylation available, but nearly all of them are concerned with organic analytical chemistry, especially gas chromatography (GC). The silylation commonly used in GC methods was applied for inorganic analytical determination of ultra-low (ng/L) levels of mercury [VIII].

Before silylation, the trace metals in the glass matrix had to be removed by cleaning with acid [50]:

1. The glassware was placed in a 1 mol/L HCl or HNO_3 solution and soaked overnight.
2. The acid solution was decanted and the glassware was rinsed thoroughly with deionised water followed by methanol.
3. The glassware was dried at 100–150 °C.

Rood suggested using 10% (v/v) dimethyldichlorosilane in toluene for silylation of injector lines [50]. In this study, 5% (v/v) solution was used according to Rapsomanikis et al. [51] and Fisher et al. [52]. Silylation was performed as follows:

1. The silylation reagent was poured into a large container equipped with a cap.
2. The glassware was placed into the container.

3. The container was sealed and the glassware was let to stand for at least 8 h at room temperature.
4. The glassware was removed from the solution and thoroughly rinsed with toluene and methanol.
5. The glassware was dried at 75–100 °C.

It is very important to rinse carefully the excess silylating reagent from the glassware before use, because residual reagent may cause a high baseline signal or noise that often requires hours to stabilise[50]. Before resilylating the glassware, the cleaning procedure has to be done according to the cleaning instructions described above.

By using the approach of the silylation technique, which is common in, for example, chromatographic methods in organic analytical chemistry, it was possible in the normal laboratory room to achieve the stability and low blank level that are essential to analytics of mercury at ng/L concentration level. It was suspected that sample vessels and their inner surfaces were initially slightly contaminated by mercury causing higher background signals. After silylation the surfaces of the vessels were “protected” and inactivated, thus preventing surface of the vessel to contribute with the sample, which resulted in lower background levels.

With the silylation reagent the free silanol groups of the glassware are able to form an inert surface suitable for ultra-low level mercury analytics. The effect of silylation was observed to last for approximately one month depending on the intensity of glassware usage. If any acidic solutions were stored in the vessels, the resilylation had to be done more frequently [VIII].

Compared with the results obtained with nonsilylated vessels, better stability of the signals, higher linearity of the calibration curves and lower blank values were obtained after silylation (see Figure. 18, [VIII]).

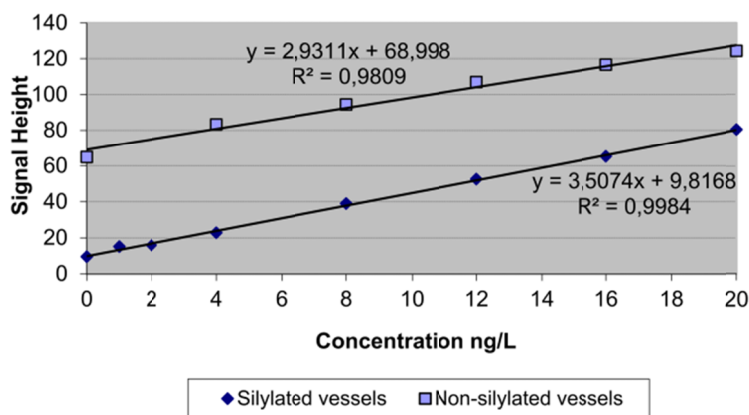


Figure 18. Calibration curves determined from the samples prepared in silylated and nonsilylated vessels [VIII]

However, it is particularly stressed that silylation itself does not solve all contamination problems encountered in trace element analytics – e.g. contamination by reagents, dust, etc. Special attention has to be given, of course, to good laboratory practices, that is analysts have to wear clean room clothes, gloves and masks [53].

The silylation technique could also be useful for determinations of other metals at ultra-low levels when the analysis is prone to contamination from the glassware. However, to achieve lower blank values, good laboratory practices are the most important factor to be carried out.

5 CONCLUSIONS

The present work introduced a set of new tools for water quality monitoring. The tools are aimed for both laboratory and field measurements of water chemical parameters. The tools included a variety of approaches for enhancing the quality of analytical results.

Computer software packages for estimation of measurement uncertainty assisting laboratories and field measurement operators have been created. It was noticed the usage of MUKIT software enabled unification of estimation of measurement uncertainty between laboratories. Although laboratories were observed to need more education in measurement uncertainty evaluations, the comparability of measurement results between laboratories is improved, when their uncertainty estimates are more comparable. At the same time measurement uncertainties estimated in different laboratories are improved when the number of under- and overestimations of measurement uncertainties is reduced. This will also lead to better usability of the measurement results for decision-making processes.

The anticipated pressure for utilisation of field sensors *in situ* in water monitoring requires immediate actions in setting up tools for assessment of the quality of data produced by these instruments. Quality assurance data of the results of sensors are necessary to collect before sensors can be used on a larger scale in national environmental monitoring programmes. Measurement uncertainty estimation is particularly lacking for sensor measurements. In this study, first time ever, it was presented for the field sensor on-line measurement a real-time uncertainty estimation procedure and a software tool, where calculations are based on Nordtest approach. This AutoMUKIT software tool is showing the way for improving the quality and comparability of the sensor measurement results.

Knowledge about the expanded measurement uncertainties has a key position for the usefulness of the results. Estimation of the measurement uncertainty will give user information on sources of random variation and bias of the method, which is highly important during the method development

Pressures to streamline water quality monitoring require seeking new ways to provide environmental data. Performance-based requirements allow using methods that are validated and proved to produce reliable measurement results for particular case. This approach will enable also the use of field and on-line measurements for monitoring purposes. SYKE has recently published quality recommendations for laboratories producing and delivering environmental monitoring data to water quality registers in Finland. Recommendations include the accreditation of the methods as well as minimum criteria for limits of quantification and measurement uncertainties.

According to the results of field PT for sensor measurement presented in this study, some of the participants performed very well. After they have successfully validated, and preferably accredited or certified, their methods as well as established internal and external quality assurance protocols (X-charts,

R-charts, proficiency test schemes etc.), these participants could produce information for water quality monitoring purposes as well.

A new way to collect environmental data is “crowdsourcing” – involving the third sector in monitoring. The present configuration of a new turbidity measuring system (Secchi3000) validated in this study was not yet fully suitable for official monitoring, but it could already enable the involvement of the third sector in the monitoring of water quality and this way citizens' observations could serve at least as supplementary information for reporting and surveys.

The toolbox presented in this study included also individual examples to improve the reliability of analytical results by enhanced quality control procedures. These include an application of “in-house” reference material for DO concentration measurement, application of enriched stable ^{196}Hg isotope for monitoring the stability of total mercury in water samples as well as silylation procedure for minimising interference effects caused by mercury losses and contamination.

The presented tools are concrete and many of them are fairly easy to apply same time enabling new ways to produce monitoring data and raising the level of quality of environmental monitoring. In order to improve the quality of analytical results, also the systematic knowledge transfer for laboratories and sensor operators is needed for both quality control procedures and measurement uncertainty estimation. The feedback received from routine laboratories has been very positive both nationally and internationally, especially regarding to the software for measurement uncertainty estimation.

6 SUMMARY

Internationally, the comparability of measurement results is remarkably important both to decision makers and the business community and the matter is of great economic importance. A vast number of important decisions – many of them industrial or environment-related – are based on measurement results. The reliability and comparability of the analytical results can be improved by realistic uncertainty estimates and by ensuring the traceability of analytical results.

The state of waters is monitored in European Union from the perspectives of water resources management, environmental protection and environmental awareness. Water resources management carried out under the EU's water policy and national acts on water resource management require knowledge of the chemical and ecological state of waters and measures for achieving good water status. In order to assess the development of the state of waters, monitoring must be arranged with a system that ensures the high quality of monitoring.

Chemical monitoring of the water bodies is usually carried out using standardised methods ensuring the high quality and comparability of the results to fulfill national water regulations. On the other hand, there is a global trend in monitoring measurements to move away from standard-based requirements and towards performance-based requirements. Performance-based requirements allow using non-standardised methods that are validated and proved to produce reliable measurement results. Pressures to streamline monitoring have grown in the state administration, mainly for economic reasons. The Ministry of the Environment in Finland drew up a monitoring strategy for the period until 2020 and set a target that included utilisation of new technologies in the collection of monitoring data. On-line measurements, remote sensing and modelling are considered preferred methods.

This work introduces a set of new tools for water quality monitoring. These include tutorial computer software aimed for chemical laboratories for estimation of measurement uncertainty mainly based on the approach described in Nordtest TR 537. Also a novel tool for a real-time uncertainty estimation procedure of a field sensor on-line measurement is presented.

The toolbox includes also individual examples to improve the reliability of analytical results by enhanced quality control procedures. For dissolved oxygen concentration measurement, an in-house reference material can be used to promote the estimation of measurement uncertainty. For mercury, enriched stable ^{196}Hg isotope is applied for monitoring the stability of total mercury in water samples. A glass surface silylation procedure is applied for minimising mercury losses and contamination.

Proper organisation of proficiency tests for field sensor measurements of selected inorganic parameters was investigated. One of the tools for future water quality monitoring is based on crowdsourcing, where citizens' observations are applied. This trend is promoted by validating an innovative measuring system (Secchi3000) for water turbidity field measurements.

7 SUMMARY IN ESTONIAN

Uudsed keemilise analüüsi „tööriistad” vete monitooringuks väli- ja laboritingimustes

Mõõtetulemuste kvaliteedi ja rahvusvahelise võrreldavuse saavutamine on märkimisväärselt oluline nii riiklike struktuuride kui ka eraettevõtete jaoks. Suur hulk olulisi igapäevaseid otsuseid põhineb mõõtetulemustel. Mõõtetulemuste võrreldavust on võimalik saavutada tagades mõõtetulemuste jälgitavuse ning omistades neile realistlikud mõõtemääramatuse hinnangud.

Euroopa Liidus monitooritakse vete seisundit ressursside parema haldamise, keskkonnakaitse ja -teadlikkuse seisukohast. See toimub EL veepoliitika ja liikmesriikide seadusandluse raames. Selleks, et monitoorimine täidaks oma eesmärgi, peavad saadavad tulemused olema kvaliteetsed.

Keemiliste parameetrite määramine veekogudes toimub enamasti standard-metoodikaid kasutades. Samas on üldine trend praegu eemaldada standardi-põhistest nõudmistest ja liikuda üha enam metoodikate suutlikkuse-põhiste nõud-miste suunas. Suutlikkuse-põhised nõudmised võimaldavad kasutada ka mitte-standardseid metoodikaid, kui nad vaid on konkreetse kasutusvaldkonna jaoks valideeritud. Teiseks trendiks on monitoorimise kuluefektiivsuse tõusu taotlemine. Andmeid on vaja märksa rohkem, kui praegu kogutakse, aga ei soovita, et sellega kaasneks märkimisväärne kulude kasv. Selle olukorra saavutamiseks on vaja kasutada enam on-line mõõtmisi, distantismõõtmisi ja modelleerimist.

Käesolevas töös pakutakse välja rida „tööriistu“ veekvaliteedi monitoorimiseks. Loodud on tarkvara mõõtemääramatuse hindamiseks nn Nordtest'i metodoloogia abil, samuti reaajas mõõtemääramatuse hindamiseks. Lahustunud hapniku sisal-duse määramiseks on välja pakutud vee küllastamisel põhinev referentsmaterjal. Elavhõbeda määramiseks on välja pakutud ¹⁹⁶Hg isotoobil põhinev sisestandard ning kasutatavate klaasnõude pinna silüeerimine.

Pädevuskatsed on väga olulised mõõtetulemuste kvaliteedi tagamisel. Töös on uuritud nende korraldamise parimaid mooduseid. Üks tuleviku jaoks olulisi lähenemisi monitoorimisel on nn „crowdsourcing”, mis põhineb kodanike kaasamisel keskkonnamonitooringusse. Seda trendi edendab käesoleva töö raames välja arendatud innovatiivne hägususe mõõtesüsteem.

8 SUMMARY IN FINNISH

Uusia kemian analytiikan työkaluja veden laadun seurantaan – Kentältä laboratorioon

Mittaustulosten vertailtavuus on kansainvälisesti erittäin tärkeää niin päätöksentekijöille kuin liike-elämälle ja asialla on suuri taloudellinen merkitys. Lukuisat tärkeät teollisuuteen tai ympäristöön liittyvät päätökset perustuvat mittaustuloksiin. Analyysitulosten luotettavuutta ja vertailukelpoisuutta voidaan parantaa realistisella mittausepävarmuuden arvioinnilla ja varmistamalla mittaustulosten jäljitettävyyden.

Vesien tilaa seurataan Euroopan unionin alueella vesivarojen hallinnan, ympäristösuojelun ja ympäristötietoisuuden näkökulmista. EU:n vesipolitiikan mukainen vesivarojen hallinta ja kansalliset säädökset edellyttävät tietoa vesien kemiallisesta ja ekologisesta tilasta sekä toimia hyvän tilan saavuttamiseksi. Jotta vesien tilan kehitystä voidaan arvioida, tulee seurantaan käyttää menetelmiä, jotka takaavat seurantatulosten korkean laadun.

Analyysitulosten korkean laadun ja vertailukelpoisuuden vuoksi sekä kansallisten määräysten täyttämiseksi, vesistöjen kemiallista seuranta toteutetaan yleensä standardisoiduilla menetelmillä. Toisaalta seurantamittauksissa ollaan maailmanlaajuisesti siirtymässä standardeihin pohjautuvista vaatimuksista menetelmien suorituskykyyn perustuviin vaatimuksiin. Suorituskykyyn perustuvat vaatimukset mahdollistavat myös sellaisten ei-standardoitujen menetelmien käytön, jotka ovat validoituja ja joiden on todettu tuottavan luotettavia mittaustuloksia. Paineet seuran tehostamiseksi ovat kasvaneet valtionhallinnossa lähinnä taloudellisista syistä. Suomen ympäristöministeriö on laatinut seurantastrategian vuoteen 2020 ja asettanut tavoitteeksi uusien teknologioiden hyödyntämiseen seurantatietojen keräämisessä. On-line mittauksia, kaukokartoitusta ja mallinnusta pyritään lisäämään.

Tässä työssä esitetään joukko uusia välineitä veden laadun seurantaan. Näitä ovat kemian laboratorioille suunnattu tietokoneohjelma mittausepävarmuuden laskentaan, joka perustuu Nordtestin mittausepävarmuusoppaassa TR 537 kuvattuun laskentatapaan. Lisäksi maastossa antureilla suoritettaville on-line mittauksille kehitettiin reaaliaikainen mittausepävarmuuden arviointimenettely ja tietokoneohjelma.

Työkaluina esitetään myös yksittäisiä esimerkkejä menetelmistä mittaustulosten luotettavuuden parantamiseksi. Näitä ovat "in-house" vertailumateriaalin käyttö mittausepävarmuuden laskennan tukena veteen liuenneen hapen määrittämisessä, rikastetun ¹⁹⁶Hg-isotoopin käyttö vesinäytteiden elohopean säilyvyystutkimuksissa sekä näyteastioiden lasipintojen silylointi elohopeahäviöiden minimoimiseksi ja kontaminaation estämiseksi.

Lisäksi tiettyjen epäorgaanisten parametrien osalta tutkittiin pätevyyskokeiden järjestämistä maastossa suoritettaville veden laadun anturimittauksille. Yksitutkituista tulevaisuuden välineistä perustuu kansalaisten havaintojen hyödyntämiseen veden laadun seurannassa. Tätä suuntausta edistettiin validoimalla innovatiivinen mittausjärjestelmä (Secchi3000) veden sameuden kenttämittauksiin.

9 REFERENCES

1. DG-Research GROWTH Programme Contract No: G6MA-2000-2002; Geoffrey Williams et al., Pembroke College, Oxford, 2002
2. Education in Metrology in Chemistry – why and how? Presented at the Finnish Laboratory Days in 2011. Available via www.ut.ee/ams/wp-content/uploads/2011/09/MiC_Education_SYKE_Helsinki_Ivo_Leito_2011.pdf
3. NIST news release (2000) New National Standards Strategy Can Advance U.S. Technology Interests. Available via www.nist.gov/public_affairs/releases/n00-14.cfm
4. ISO (1993) Guide To The Expression Of Uncertainty In Measurement (GUM), Geneva, Switzerland (Reprinted 1995)
5. JCGM 100 (2008) Evaluation of measurement data – Guide to the expression of uncertainty in measurement (GUM)
6. Eurachem/CITAC Guide CG 4 (2012) Quantifying Uncertainty in Analytical Measurement, 3rd edition. Available via www.eurachem.org
7. Magnusson B, Näykki T, Hovind H, Krysell M (2011) Nordtest Technical Report 537 – Handbook for the calculation of measurement uncertainty in environmental laboratories, 3rd edition, Nordic Innovation, Oslo, Norway. Available via www.nordtest.info
8. Eurolab (2007) Measurement Uncertainty Revisited: Alternative Approaches to Uncertainty Evaluation. Available via www.eurolab.org/documents/Technical_Report_Measurement_Uncertainty_2007.pdf
9. ISO 11352:2012, Water quality – Estimation of measurement uncertainty based on validation and quality control data, International Standard Organization (ISO), Geneva, Switzerland, 2012
10. Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy. Available via <http://ec.europa.eu/environment/water/water-framework/>
11. 1299/2004, Act on Water Resources Management. Available via <http://www.finlex.fi/fi/laki/kaannokset/2004/en20041299.pdf>
12. 86/2000, Environmental Protection Act. Available via <http://www.finlex.fi/fi/laki/kaannokset/2000/en20000086.pdf>
13. Common Implementation Strategy for the Water Framework Directive (2000/60/EC). Technical Report – 2009 – 025 Guidance Document No. 19 Guidance on Surface Water Chemical Monitoring under the Water Framework Directive. Available via <https://circabc.europa.eu/sd/d/e54e8583-faf5-478f-9b11-41fda9e9c564/Guidance%20No%2019%20-%20Surface%20water%20chemical%20monitoring.pdf>
14. Monitoring Strategy of the State of the Environment 2020 (In Finnish), Ministry of the Environment, Helsinki 2011. Available via <http://www.ym.fi/download/noname/%7B4A092091-75FE-4090-B630-D24631212388%7D/32105>
15. Korhonen-Ylönen K, Näykki T, Leivuori M, Tervonen K, Lanteri S, Ilmakunnas M (2013) Proficiency Test SYKE 2/2013, Chlorophyll a, colour, conductivity, nutrients, pH and turbidity in natural waters. Reports of Finnish Environment Institute 20/2013, Finnish Environment Institute, Helsinki, Finland. Available via <http://www.syke.fi/download/noname/%7BF576874A-DA49-4064-B514-6FC782D0E73B%7D/56911>

16. Leivuori M, Korhonen-Ylönen K, Sara-Aho T, Näykki T, Tervonen K, Lanteri S, Ilmakunnas M (2014) Proficiency Test SYKE 4/2013 Metals in waters and sediment. Reports of Finnish Environment Institute 1/2014, Finnish Environment Institute, Helsinki, Finland. Available via <http://www.syke.fi/download/noname/%7BBCC7C4E0-925B-4637-AC59-4AE86FA7DC03%7D/95885>
17. EN ISO/IEC 17025:2005, General requirements for the competence of testing and calibration laboratories, European Committee for Standardization, 2005
18. Ellison SLR, Barwick VJ (1998) Using validation data for ISO measurement uncertainty estimation. Part 1. Principles of an approach using cause and effect analysis, *Analyst* 123:1387–1392
19. Maroto A, Riu J, Boqué R, Rius FV (1999) Estimating uncertainties of analytical results using information from the validation process, *Anal Chim Acta* 391:173–185
20. Jülicher B, Gowik P, Uhlig S (1999) A top-down in-house validation based approach for the investigation of the measurement uncertainty using fractional factorial experiments, *Analyst* 124:537
21. Silva RJNB, Lino MJ, Santos JR, Camões MFGFC (2000) Estimation of precision and efficiency mass transfer steps for the determination of pesticides in vegetables aiming at the expression of results with reliable uncertainty, *Analyst* 125:1459–1464
22. Silva RJNB, Figueiredo H, Santos JR, Camoes MFGFC (2003) Evaluation of Sample Processing and Sub-sampling Performance, *Anal Chim Acta* 477:169–185
23. Silva RJNB, Santos JR, Camões MFGFC (2006) A new terminology for the approaches to the quantification of the measurement uncertainty, *Accred Qual Assur* 10:664–671
24. ISO 21748:2010, Guidance for the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation, International Standard Organization (ISO), Geneva, Switzerland, 2010
25. Hovind H, Magnusson B, Krysell M, Lund U, Mäkinen I (2011) Nordtest Technical Report 569 – Internal Quality Control – Handbook for Chemical laboratories, 4th edition, Nordic Innovation, Oslo, Norway. Available via www.nordtest.info
26. Rasmussen SN (2003) Software tools for the expression of uncertainty in measurement, MetroTrade Workshop on Traceability and Measurement Uncertainty in Testing. Berlin, January 30–31, 2003
27. Jurado JM, Alcázar A (2005) A software package comparison for uncertainty measurement estimation according to GUM, *Accred Qual Assur* 10:373–381
28. Ellison SLR, Thompson M (2011) Dark Uncertainty, *Accred Qual Assur* 16:483–487
29. ENVICAL SYKE website: <http://www.syke.fi/envical/en>
30. Jalukse L, Vabson V, Leito I (2006) In situ interlaboratory comparisons for dissolved oxygen concentration and pH, *Accred Qual Assur* 10:562–564.
31. Jalukse L, Helm I, Leito I (2012) ESTDO-2012: Dissolved Oxygen Concentration Interlaboratory Comparison Measurement, Final Report, University of Tartu Testing Centre. Available via http://www.ut.ee/katsekoda/ILC/O2_2012/ESTDO-2012_final_report.pdf
32. Leivuori M, Björklöf K, Näykki T, Väisänen R (2013) Laboratorioiden välinen pätevyyskoe 5/2013, Kenttämittaukset -vesien happi, lämpötila, pH ja sähköjohtavuus (In Finnish), Finnish Environment Institute, Helsinki, Finland. Available via <http://www.syke.fi/download/noname/%7BFD00FB6D-21B3-4D8F-8C35-424926B9E626%7D/92086>

33. Ramsey MH, Ellison SLR (eds.) (2007) Eurachem/EUROLAB/CITAC/ Nordtest/ AMC Guide: Measurement uncertainty arising from sampling- a guide to methods and approaches. Eurachem. Available via http://www.eurachem.org/images/stories/Guides/pdf/UfS_2007.pdf
34. Helm I, Jalukse L, Leito I (2010) Measurement Uncertainty Estimation in Amperometric Sensors: A Tutorial Review, *Sensors*, 10: 4430-4455
35. Analytical Method Committee. Is My Uncertainty Estimate Realistic? AMC Technical Brief No. 15; Available via http://www.rsc.org/images/realistic-estimate-technical-brief-15_tcm18-214874.pdf
36. Näykki T, Kyröläinen H, Witick A, Mäkinen I, Pehkonen R, Väisänen T, Sainio P, Luotola M (2013) Quality recommendations for data entered into the environmental administration's water quality registers: Quantification limits, measurement uncertainties, storage times and methods associated with analytes determined from waters (In Finnish), Environmental Administration Guidelines 4/2013, Finnish Environment Institute, Helsinki, Finland. Available via <https://helda.helsinki.fi/handle/10138/40920>
37. Toivanen T, Koponen S, Kotovirta V, Molinier M, Chengyuan Peng (2013) Water quality analysis using an inexpensive device and a mobile phone, *Environmental Systems Research* 2:9
38. 1060 C. Sample Storage and Preservation, Standard methods for the examination of water and waste water (1998), American Public Health Association, American Water Works Association and Water Environment Federation, 20th edition, 1–33 – 1–35.
39. Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council
40. ISO 17852:2006, Water quality – Determination of mercury – Method using atomic fluorescence spectrometry, International Standard Organization (ISO), Geneva, Switzerland, 2006.
41. EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry; Environmental Protection Agency, United States, 2002
42. ISO 12846:2012, Water quality — Determination of mercury — Method using atomic absorption spectrometry (AAS) with and without enrichment, International Standard Organization (ISO), Geneva, Switzerland, 2012.
43. ASTM D 3223 – 12 (2013) Standard Test Method for Total Mercury in Water. Annual Book of ASTM Standards, Water and environmental technology, vol 11.01, 368–375.
44. ISO 5667-3:2012, Water quality – Sampling – Part 3: Preservation and handling of water samples; International Standard Organization (ISO), Geneva, Switzerland, 2012.
45. ASTM D 4841 – 88 (Reapproved 2008) (2013) Standard Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents. Annual Book of ASTM Standards, Water and environmental technology, vol 11.01, 603–608
46. Sargent M, Harte R, Harrington C (2002) Guidelines for Achieving High Accuracy in Isotope Dilution Mass Spectrometry (IDMS), Royal Society of Chemistry, Cambridge, United Kingdom.

47. Vogl J, Pritzkow W (2010) Isotope dilution mass spectrometry — A primary method of measurement and its role for RM certification, MAPAN-Journal of Metrology Society of India, 25(3):135–164.
48. Schiel D, Rienitz O (2011) Final report on CCQM-K70: Determination of Hg in natural water at a concentration level required by the European environmental quality standard (EQS), Metrologia, 48(1A), 08011
49. Leermakers M, Lansens P, Baeyens W (1990) Storage and stability of inorganic and methylmercury solutions, Fresenius J Anal Chem, 336, 655–662.
50. Rood D (1995) A practical guide to the care, maintenance, and troubleshooting of capillary gas chromatographic systems, 2nd edn. Hüthig, Heidelberg, p 153
51. Rapsomanikis S, Harrison RM (1988) Speciation of butyltin compounds in oyster samples, Appl Organomet Chem, 2:151–157
52. Fischer R, Rapsomanikis S, Andreae MO (1993) Determination of methylmercury in fish samples using GC/AAS and sodiumtetraethylborate derivatization, Anal Chem 65:763–766
53. Moody JR (1982) NBS Clean Laboratories for Trace Element Analysis, Anal Chem 54:1358A–1376A

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1. Näykki T., Virtanen A., Leito I., Software support for the Nordtest method of measurement uncertainty evaluation, *Accredit Qual Assur* **2012**, 17:603–612
2. Näykki T., Koponen S., Väisänen T., Pyhälähti T., Toivanen T., Leito I., Validation of a new measuring system for water turbidity field measurements, *Accredit Qual Assur*, **2014**, 19 (3): 175–183
3. Näykki T., Jalukse L., Helm I., Leito I., Dissolved Oxygen Concentration Interlaboratory Comparison: What Can We Learn?, *Water*, **2013**, 5, 420–442.
4. Näykki T., Magnusson B., Helm I., Jalukse L., Väisänen T., Leito I., Comparison of measurement uncertainty estimates using quality control and validation data, *J Chem Metrol*, **2014**, 8 (1): 1–12
5. Näykki T., Virtanen A., Kaukonen L., Magnusson B., Väisänen T., Leito I., Software support for the Nordtest method of measurement uncertainty evaluation of field on-line turbidity measurement, submitted to *Environ Monit Assess*
6. Näykki T., Leivuori M., Björklöf K., Väisänen R., Laine M., Väisänen T., Leito I., Proficiency test of pH, Conductivity and Dissolved Oxygen Concentration Field Measurements in River Water, *Accredit Qual Assur*, **2014**, DOI 10.1007/s00769-014-1064-5
7. Näykki T., Sara-Aho T., T. Väisänen, Leito I., Application of enriched stable Hg-196 isotope for monitoring the stability of total mercury in water samples submitted to *Int J Environ Anal Chem*
8. Näykki T., The use of silylation for minimizing the interference effects caused by contamination in ultra-low level mercury analytics. *Anal Bioanal Chem*, **2002**, 372 (7): 829–831
9. Näykki, T., Perämäki, P., Kujala, J., Mikkonen, A. Optimization of a flow injection hydride generation atomic absorption spectrometric method for the determination of arsenic, antimony and selenium in iron chloride/sulfate-based water treatment chemical. *Anal Chim Acta*, **2001**, 439 (2): 229–238
10. Näykki, T., Anttila, R., Perämäki, P., Kurikka, A., Nikula, P. Determination of Na₂O from sodium aluminate NaAlO₂, *Talanta*, **2000**, 52(4): 755–760

International reports, conference publications and posters:

Measurement uncertainty revisited: Alternative approaches to uncertainty evaluation, (As a part of Eurolab expert group on measurement uncertainty), *Eurolab Technical Report No. 1/2007, March 2007*

Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories, Magnusson, B.; Näykki, T.; Hovind, H.; Krysell, M., *Report of the Nordtest project 1589-02, June 2003* (revised in 2004 and 2011)

Above mentioned handbook was awarded by CITAC as one the best publication in the world in the field of metrology in chemistry.

3. Recognitions

CITAC (Cooperation of International Traceability in Analytical Chemistry) award for one of the best publications in the field of Metrology, **2008**.

Publication: Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories

Administrative responsibilities

Member of government of Finntesting association (merger of Eurolab Finland and Eurachem-Finland associations), **2001** – present

Retraining and Updating:

JTO School of Management, **2008–2009**.

Degree: Specialist Qualification in Management

PUBLICATIONS OF TEEMU NÄYKKI

I. Publications in international journals

1. Näykki T., Virtanen A., Leito I., Software support for the Nordtest method of measurement uncertainty evaluation, *Accredit Qual Assur* **2012**, 17:603–612
2. Näykki T., Koponen S., Väisänen T., Pyhälähti T., Toivanen T., Leito I., Validation of a new measuring system for water turbidity field measurements, *Accredit Qual Assur*, **2014**, 19 (3):175–183
3. Näykki T., Jalukse L., Helm I., Leito I., Dissolved Oxygen Concentration Interlaboratory Comparison: What Can We Learn?, *Water*, **2013**, 5, 420–442.
4. Näykki T., Magnusson B., Helm I., Jalukse L., Väisänen T., Leito I., Comparison of measurement uncertainty estimates using quality control and validation data, *J Chem Metrol*, **2014**, 8 (1): 1–12
5. Näykki T., Virtanen A., Kaukonen L., Magnusson B., Väisänen T., Leito I., Software support for the Nordtest method of measurement uncertainty evaluation of field on-line turbidity measurement, submitted. *Environ Monit Assess*
6. Näykki T., Leivuori M., Björklöf K., Väisänen R., Laine M., Väisänen T., Leito I., Proficiency test of pH, Conductivity and Dissolved Oxygen Concentration Field Measurements in River Water, *Accredit Qual Assur*, **2014**, DOI 10.1007/s00769-014-1064-5

7. Näykki T., Sara-Aho T., T. Väisänen, Leito I., Application of enriched stable Hg-196 isotope for monitoring the stability of total mercury in water samples submitted to *Int J Environ Anal Chem*
8. T. Näykki, The use of silylation for minimizing the interference effects caused by contamination in ultra-low level mercury analytics. *Anal Bioanal Chem*, **2002**, 372 (7):829–831
9. Näykki, T., Perämäki, P., Kujala, J., Mikkonen, A. Optimization of a flow injection hydride generation atomic absorption spectrometric method for the determination of arsenic, antimony and selenium in iron chloride/sulfate-based water treatment chemical. *Anal Chim Acta*, **2001**, 439 (2): 229–238
10. Näykki, T., Anttila, R., Perämäki, P., Kurikka, A., Nikula, P. Determination of Na₂O from sodium aluminate NaAlO₂, *Talanta*, **2000**, 52(4): 755–760

II. International reports, conference publications and posters

1. Validation of Secchi3000 fieldanalyser for water turbidity measurements. Näykki, T.; Koponen, S.; Leito, I. *Poster in FMTDK conference, March 2013, Tallinn, Estonia*
2. Improving Comparability of Analytical Results with Practical Software for Estimating Measurement Uncertainty. Näykki, T.; Virtanen, A.; Leito, I. *Poster in FMTDK conference, February 2012, Tartu, Estonia*
3. Improving Comparability of Analytical Results with Practical Software for Estimating Measurement Uncertainty. Näykki, T.; Virtanen, A.; Leito, I. *Poster in Eurachem workshop, 6–8 June 2011, Lisbon, Portugal*
4. Measurement uncertainty revisited: Alternative approaches to uncertainty evaluation, (As a part of Eurolab expert group on measurement uncertainty), *Eurolab Technical Report No. 1/2007, March 2007*
5. Nordtest Handbook for Calculation of Measurement Uncertainty Based on Quality Control and Method Validation. Magnusson, B.; Näykki, T.; Hovind, H.; Krysell, M. *Poster in The First International Proficiency Testing Conference, 11–13 October, 2007 Sinaia, Romania.*
6. Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories, Magnusson, B.; Näykki, T.; Hovind, H.; Krysell, M., *Report of the Nordtest project 1589-02, June 2003* Above mentioned handbook was awarded by CITAC as one the best publication in the world in the field of metrology in chemistry.
7. Effects of different pretreatment procedures for analysis of mercury from industrial wastewater. Näykki, T.; Huhtala, S.; Mäkinen, I. *Poster in First Baltic Symposium on Environmental Chemistry. 26–29 September 2001. Tartu, Estonia.*

III. Other publications

Articles in professional magazines (In Finnish)

1. Näykki, T., *Laatua laboratoriomäärityksiin*, Kemia Kemi (2013) 4:52–53
2. Väisänen T., Näykki T., Luotola M. *Ympäristöseurannan menestystekijät tulevaisuudessa – SYKE:n laboratorion rooli*, Vesitalous (2013) 2, Helsinki
3. Näykki, T. *Mittausepävarmuuden arviointi ympäristölaboratoriossa*, Analyysi 2007 44 (4):7
4. Näykki, T. *Ympäristönäytteiden analyysimenetelmien validointi*, Analyysi 2007; 44 (4):6
5. Näykki, T. *Näyteastioiden valinta pienten metallipitoisuuksien määrittämisessä*, Analyysi 2004 41(4): 8–13.

Professional reports

1. Laboratorioiden välinen pätevyyskoe 10/2013. Ravinteet, kloridi, pH, sulfaatti ja sähkönjohtavuus jätevesistä, Kaija Korhonen-Ylönen, Mirja Leivuori, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Ritva Väisänen, Helsinki: Suomen ympäristökeskus, **2014**.
2. Laboratorioiden välinen pätevyyskoe SYKE 7/2013: Talousvesimääritykset, Kaija Korhonen-Ylönen, Teemu Näykki, Mika Sarkkinen, Timo Sara-Aho, Mirja Leivuori, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Ritva Väisänen, Helsinki: Suomen ympäristökeskus, **2014**.
3. Laboratorioiden välinen pätevyyskoe. Uima-allasvesivertailu, Mirja Leivuori, Sami Tyrväinen, Kaija Korhonen-Ylönen, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Helsinki: Suomen ympäristökeskus, **2014**.
4. Proficiency test SYKE 4/2013. Metals in water and sediment, Mirja Leivuori, Kaija Korhonen-Ylönen, Timo Sara-Aho, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas Helsinki: Suomen ympäristökeskus, **2014**.
5. Laboratorioiden välinen pätevyyskoe 1/2013: Uima-allasvesivertailu. Kaija Korhonen-Ylönen, Sami Tyrväinen, Mirja Leivuori, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2013**.
6. Laboratorioiden välinen pätevyyskoe 11/2012. Alkaliniteetti, ravinteet, pH, sähkönjohtavuus ja väri jätevesistä. Kaija Korhonen-Ylönen, Teemu Näykki, Mirja Leivuori, Keijo Tervonen, Sari Lanteri, Ilmakunnas, Markku, Ritva Väisänen. Helsinki: Suomen ympäristökeskus, **2013**.
7. Laboratorioiden välinen pätevyyskoe 3/2013. Katarina Björklöf, Kaija Korhonen-Ylönen, Teemu Näykki, Marketta Turunen, Timo Sara-aho, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Helsinki: Suomen ympäristökeskus, **2013**.
8. Proficiency test SYKE 5/2012. Metals in waters and soil. Mirja Leivuori, Kaija Korhonen-Ylönen, Timo Sara-Aho, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2013**.

9. Laboratorioiden välinen pätevyyskoe 1/2012: Alkaliniteetti, pH, ravinteet ja sähkönjohtavuus luonnonvesistä. Kaija Korhonen-Ylönen, Mirja Leivuori, Teemu Näykki, Olli Järvinen, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Ritva Väisänen. Helsinki: Suomen ympäristökeskus, **2012**.
10. Laboratorioiden välinen pätevyyskoe 2/2012: Uima-allasvertailu. Kaija Korhonen-Ylönen, Sami Tyrväinen, Mirja Leivuori, Teemu Näykki, Olli Järvinen, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Ritva Väisänen. Helsinki: Suomen ympäristökeskus, **2012**.
11. Laboratorioiden välinen pätevyyskoe 3/2012: BOD7, CODCr, CODMn, kiintoaine, Na ja TOC jätevesistä. Kaija Korhonen-Ylönen, Mirja Leivuori, Teemu Näykki, Marketta Turunen, Olli Järvinen; Timo Sara-aho, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Ritva Väisänen. Helsinki: Suomen ympäristökeskus, **2012**.
12. Laboratorioiden välinen pätevyyskoe 4/2012: Happi, a-klorofylli, saliniteetti, SiO₂, TIC ja TOC luonnonvesistä. Kaija Korhonen-Ylönen, Mirja Leivuori, Marketta Turunen, Teemu Näykki, Olli Järvinen, Mika Sarkkinen, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Ritva Väisänen. Helsinki: Suomen ympäristökeskus, **2012**.
13. Laboratorioiden välinen pätevyyskoe 7/2012: Talousvesimääritykset. Kaija Korhonen-Ylönen, Teemu Näykki, Mika Sarkkinen, Timo Sara-Aho, Olli Järvinen, Mirja Leivuori, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Ritva Väisänen. Helsinki: Suomen ympäristökeskus, **2012**.
14. Proficiency Test SYKE 10/2011: Heavy metals in surface waters. Mirja Leivuori, Kaija Korhonen-Ylönen, Timo Sara-Aho, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Helsinki: Suomen ympäristökeskus, **2012**.
15. Verkostomainen yhteistyö ympäristöhallinnon laboratoriotoiminnan menestystekijänä, Marja Luotola, Riitta Pehkonen, Teemu Näykki, Tero Väisänen, Helsinki: Suomen ympäristökeskus, **2012**.
16. Laboratorioiden välinen pätevyyskoe 9/2011: ravinteet, kloridi, pH, sulfaatti ja sähkönjohtavuus jätevesistä. Kaija Korhonen-Ylönen, Mirja Leivuori, Teemu Näykki, Olli Järvinen, Mika Sarkkinen, Sari Lanteri, Markku Ilmakunnas ja Ritva Väisänen Helsinki: Suomen ympäristökeskus, **2012**.
17. The effect of gypsum on phosphorus losses at the catchment scale. Petri Ekholm, Elina Jaakkola, Mikko Kiirikki, Kirsti Lahti, Jouni Lehtoranta, Visa Mäkelä, Teemu Näykki, Liisa Pietola, Sirkka Tattari, Pasi Valkama, Ljudmila Vesikko and Sari Väisänen Helsinki: Finnish Environment Institute, **2011**.
18. Laboratorioiden välinen pätevyyskoe 2/2011: BOD7, CODCr, CODMn, kiintoaine, Na ja TOC jätevesistä. Kaija Korhonen-Ylönen, Mirja Leivuori, Teemu Näykki, Olli Järvinen, Timo Sara-Aho, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas ja Ritva Väisänen Helsinki: Suomen ympäristökeskus, **2011**.

19. Laboratorioiden välinen pätevyyskoe 1/2011: a-klorofylli, pH, ravinteet, sameus, sähkönjohtavuus ja väri luonnonvesistä. Kaija Korhonen-Ylönen, Teemu Näykki, Olli Järvinen, Mirja Leivuori, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas ja Ritva Väisänen, Helsinki: Suomen ympäristökeskus, **2011**.
20. Laboratorioiden välinen pätevyyskoe 5/2011: talousvesimääritykset. Kaija Korhonen-Ylönen, Mika Sarkkinen, Teemu Näykki, Timo Sara-Aho, Olli Järvinen, Mirja Leivuori, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas ja Ritva Väisänen Helsinki: Suomen ympäristökeskus, **2011**.
21. Laboratorioiden välinen pätevyyskoe 7/2010: ravinteet, pH ja sähkönjohtavuus jätevedestä sekä happimääritys rannikko- ja järvivedestä. Kaija Korhonen, Mirja Leivuori, Teemu Näykki, Olli Järvinen, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas ja Ritva Väisänen Helsinki: Suomen ympäristökeskus, **2011**.
22. Proficiency test SYKE 3/2011: metals in water and sludge. Mirja Leivuori, Kaija Korhonen-Ylönen, Timo Sara-Aho, Teemu Näykki, Keijo Tervonen, Sari Lanteri and Markku Ilmakunnas, Helsinki: Finnish Environment Institute, **2011**.
23. Laboratorioiden välinen pätevyyskoe 1/2010: alkaliniteetti, ravinteet, pH ja sähkönjohtavuus luonnonvesissä Kaija Korhonen, Teemu Näykki, Olli Järvinen, Mirja Leivuori, Keijo Tervonen, Markku Ilmakunnas ja Sari Lanteri. Helsinki: Suomen ympäristökeskus, **2010**.
24. Laboratorioiden välinen pätevyyskoe 2/2010: BOD7, CODCr, CODMn, kiintoaine, Na ja TOC jätevesistä. Kaija Korhonen, Teemu Näykki, Olli Järvinen, Timo Sara-Aho, Mirja Leivuori, Keijo Tervonen, Sari Lanteri ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2010**.
26. Laboratorioiden välinen pätevyyskoe 4/2010: klorofylli a, saliniteetti, SiO₂, ja TOC luonnonvesistä. Kaija Korhonen, Olli Järvinen, Teemu Näykki, Mirja Leivuori, Keijo Tervonen, Sari Lanteri ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2010**.
27. Laboratorioiden välinen vertailukoe 6/2010: talousvesimääritykset. Kaija Korhonen, Teemu Näykki, Olli Järvinen, Timo Sara-Aho, Mirja Leivuori, Keijo Tervonen, Sari Lanteri ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2010**.
28. Laboratorioiden välinen pätevyyskoe 9/2009: ravinteet, pH, sähkönjohtavuus, kloridi ja sulfaatti jätevesistä. Mirja Leivuori, Kaija Tervonen, Olli Järvinen, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas ja Ritva Väisänen. Helsinki: Suomen ympäristökeskus, **2010**.
29. Laboratorioiden välinen pätevyyskoe 1/2009: a-klorofylli, BOD7, CODMn, ravinteet, sameus, TOC ja väri luonnonvesistä. Kaija Korhonen, Teemu Näykki, Olli Järvinen, Keijo Tervonen, Sari Lanteri ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2009**.
30. Laboratorioiden välinen pätevyyskoe 3/2009 BOD7, CODDCr, CODMn, kiintoaine, Na ja TOC jätevesistä. Kaija Korhonen, Mirja Leivuori, Teemu

- Näykki, Olli Järvinen, Timo Sara-Aho, Keijo Tervonen, Sari Lanteri, ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2009**.
31. Laboratorioiden välinen pätevyyskoe 6/2008: metallit vedestä ja lietteestä. Kaija Korhonen, Olli Järvinen, Teemu Näykki, Timo Sara-aho, Raija Ivalo, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2009**.
 32. Laboratorioiden välinen pätevyyskoe 7/2008: talousvesimääriytykset. Kaija Korhonen, Teemu Näykki, Olli Järvinen, Timo Sara-Aho, Keijo Tervonen, Markku Ilmakunnas ja Sari Lanteri. Helsinki: Suomen ympäristökeskus, **2009**.
 33. Laboratorioiden välinen pätevyyskoe 9/2008: AOX, pH, ravinteet, sameus, sähkönjohtavuus ja väri jätevesistä. Kaija Korhonen, Teemu Näykki, Olli Järvinen, Lea Kervinen, Keijo Tervonen, Markku Ilmakunnas ja Sari Lanteri. Helsinki: Suomen ympäristökeskus, **2009**.
 34. Laboratorioiden välinen pätevyyskoe 4/2007: metallit ja elohopea vesistä, maasta ja sedimentistä sekä typpi, fosfori, pH, rikki ja TOC lietteestä. Irma Mäkinen, Olli Järvinen, Teemu Näykki, Timo Sara-Aho, Raija Ivalo, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2008**.
 35. Laboratorioiden välinen pätevyyskoe 7/2007: alkaliniteetti, kloridi, pH, sähkönjohtavuus, sulfaatti ja ravinteet jätevesistä. Kaija Korhonen, Olli Järvinen, Teemu Näykki, Tero Eklun, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2008**.
 36. Laboratorioiden välinen pätevyyskoe 2/2007: alkaliniteetti, BOD7, happi, pH, ravinteet, sameus, sähkönjohtavuus, TOC ja väri. Kaija Korhonen, Olli Järvinen, Teemu Näykki, Irma Mäkinen, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2007**.
 37. Laboratorioiden välinen pätevyyskoe 3/2007 BOD7, COD, COD, kiintoaine, Na, sameus, TOC ja väri jätevesistä. Korhonen, Kaija, Näykki, Teemu, Järvinen, Olli, Sara-Aho, Timo, Mäkinen, Irma, Tervonen, Keijo, Ilmakunnas, Markku. Helsinki: Suomen ympäristökeskus, **2007**.
 38. Laboratorioiden välinen pätevyyskoe 6/2006. Metallit ja elohopea vesistä ja lietteestä. Irma Mäkinen, Olli Järvinen, Teemu Näykki, Timo Sara-Aho, Raija Ivalo, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2007**.
 39. Laboratorioiden välinen pätevyyskoe 8/2006: alkaliniteetti, kiintoaine, kloridi, pH, sähkönjohtavuus, sulfaatti ja ravinteet jätevesistä. Kaija Korhonen, Irma Mäkinen, Olli Järvinen, Teemu Näykki, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2007**.
 40. Laboratorioiden välinen pätevyyskoe 4/2005: metallit ja elohopea vesistä ja maasta. Irma Mäkinen, Olli Järvinen, Teemu Näykki, Timo Sara-Aho, Raija Ivalo, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2006**.
 41. Laboratorioiden välinen pätevyyskoe 4/2006: a-klorofylli, happi, saliniteetti ja silikaatti (SiO₂) luonnonvedestä. Kaija Korhonen, Irma Mäkinen,

- Teemu Näykki, Olli Järvinen, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2006**.
42. Laboratorioiden välinen pätevyyskoe 5/2005: talousvesimääritykset. Irma Mäkinen, Olli Järvinen, Kaija Korhonen, Teemu Näykki, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2006**.
 43. Laboratorioiden välinen pätevyyskoe 6/2005: NNH_4 , NNO_3+NO_2 , N_{tot} , PPO_4 , P_{tot} , pH, sähkönjohtavuus ja kiintoaine jätevesistä. Mäkinen, Irma, Korhonen, Kaija, Näykki, Teemu, Järvinen, Olli, Tervonen, Keijo, Ilmakunnas, Markku. Helsinki: Suomen ympäristökeskus, **2006**.
 44. Laboratorioiden välinen pätevyyskoe 7/2006: talousvesimääräykset. Kaija Korhonen, Irma Mäkinen, Olli Järvinen, Timo Sara-Aho, Teemu Näykki, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2006**.
 45. Laboratorioiden välinen vertailukoe 1/2006: ravinteet, sameus ja väri luonnonvesistä. Kaija Korhonen, Irma Mäkinen, Teemu Näykki, Olli Järvinen, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2006**.
 46. Laboratorioiden välinen pätevyyskoe 1/2005 pH, sähkönjohtavuus, alkaliniteetti, BOD, ravinteet, Na, K, Ca, Mg, happi, TOC, sameus ja väri luonnonvesissä. Irma Mäkinen, Kaija Korhonen, Teemu Näykki, Olli Järvinen, Keijo Tervonen, Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2005**.
 47. Laboratorioiden välinen pätevyyskoe 3b/2004; Epäorgaaniset yhdisteet vedestä. Irma Mäkinen, Olli Järvinen, Kaija Korhonen, Teemu Näykki ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2005**.
 48. Laboratorioiden välinen pätevyyskoe 6/2004; Talousvesimääritykset. Irma Mäkinen, Olli Järvinen, Teemu Näykki, Kaija Korhonen, Keijo Tervonen, Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2005**.
 49. Laboratorioiden välinen pätevyyskoe 7/2004; ravinteet, pH, sähkönjohtavuus ja kiintoaine jätevesistä. Irma Mäkinen, Kaija Korhonen, Teemu Näykki, Olli Järvinen, Keijo Tervonen, Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2005**.
 50. Laboratorioiden välinen pätevyyskoe 1/2004: (ravinteet, happi, silikaatti, saliniteetti ja a-klorofylli luonnonvesistä). Irma Mäkinen, Sami Huhtala, Olli Järvinen, Kaija Korhonen, Teemu Näykki, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2004**.
 51. Laboratorioiden välinen pätevyyskoe 5/2003: metallit ja elohopea vesistä ja maasta. Irma Mäkinen, Sami Huhtala, Olli Järvinen, Teemu Näykki ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2004**.
 52. Laboratorioiden välinen pätevyyskoe 6/2003: määritykset talousvesistä. Irma Mäkinen, Sami Huhtala, Kaija Korhonen, Teemu Näykki, Olli Järvinen, Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2004**.
 53. Laboratorioiden välinen pätevyyskoe 7/2003 Nnh_4 , Nno_3+NO_2 , N_{tot} , Ppo_4 , P_{tot} , sähkönjohtavuus ja kiintoaine jätevesissä. Irma Mäkinen, Sami

- Huhtala, Olli Järvinen, Kaija Korhonen, Teemu Näykki, Keijo Tervonen, Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2004**.
54. Laboratorioiden välinen pätevyyskoe 1/2003: ravinteet, kiintoaine, TOC, väri ja sameus luonnonvesissä. Irma Mäkinen, Sami Huhtala, Olli Järvinen, Kaija Korhonen, Teemu Näykki ja Pasi Salonen. Helsinki: Suomen ympäristökeskus, **2003**.
 55. Laboratorioiden välinen pätevyyskoe 8/2002: Ravinteet ja kiintoaine jätevesistä. Irma Mäkinen, Sami Huhtala, Kaija Korhonen, Teemu Näykki, Pasi Salonen. Helsinki: Suomen ympäristökeskus, **2003**.
 56. Laboratorioiden välinen vertailukoe 6/2002: pH, alkaliniteetti, sähkönjohtavuus, Cl, F, SO₄, COD Mn, Kovuus, N NO₂, N NO₃, N NH₄. Irma Mäkinen, Sami Huhtala, Kaija Korhonen, Teemu Näykki, Olli Järvinen ja Pasi Salonen. Helsinki: Suomen ympäristökeskus, **2003**.
 57. Laboratorioiden välinen vertailukoe 1/2002: pH, sähkönjohtavuus, alkaliniteetti, Na, K, Ca, Mg, SO₄, Cl, BOD₇, NNH₄⁺, NNO₂+NO₃⁻, Ntot, PPO₄ ja Ptot. Irma Mäkinen, Sami Huhtala, Kaija Korhonen, Teemu Näykki, Olli Järvinen, Pasi Salonen ja Mia Aalto. Helsinki: Suomen ympäristökeskus, **2002**.
 58. Laboratorioiden välinen vertailukoe 3/2001. Irma Mäkinen, Sami Huhtala, Olli Järvinen, Teemu Näykki ja Pasi Salonen. Helsinki: Suomen ympäristökeskus, **2002**.
 59. Laboratorioiden välinen vertailukoe 3/2002: a-klorofylli, silikaatti (SiO₂), orgaaninen hiili (TOC) ja saliniteetti. Irma Mäkinen, Sami Huhtala, Kaija Korhonen, Teemu Näykki, Olli Järvinen, Pasi Salonen ja Miia Aalto. Helsinki: Suomen ympäristökeskus, **2002**.
 60. Laboratorioiden välinen vertailukoe 4/2001. Irma Mäkinen, Sami Huhtala, Kaija Korhonen, Teemu Näykki, Olli Järvinen ja Pasi Salonen. Helsinki: Suomen ympäristökeskus, **2002**.
 61. Laboratorioiden välinen vertailukoe 6/2001. Irma Mäkinen, Sami Huhtala, Kaija Korhonen, Teemu Näykki, Pasi Salonen. Helsinki: Suomen ympäristökeskus, **2002**.
 62. Laboratorioiden välinen vertailukoe 1/2001. Irma Mäkinen, Sami Huhtala, Kaija Korhonen, Olli Järvinen, Teemu Näykki ja Pasi Salonen. Helsinki: Suomen ympäristökeskus, **2001**.
 63. Laboratorioiden välinen vertailukoe 4/2000. Irma Mäkinen, Sami Huhtala, Olli Järvinen, Teemu Näykki ja Timo Vänni. Helsinki: Suomen ympäristökeskus, **2001**.
 64. Laboratorioiden välinen vertailukoe 6/2000. Irma Mäkinen, Sami Huhtala, Kaija Korhonen, Teemu Näykki, Pasi Salonen. Helsinki: Suomen ympäristökeskus, **2001**.

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Olulisimad publikatsioonid:

Publikatsioonid rahvusvahelistes ajakirjades

1. Näykki T., Virtanen A., Leito I., Software support for the Nordtest method of measurement uncertainty evaluation, *Accredit Qual Assur* **2012**, 17:603–612
2. Näykki T., Koponen S., Väisänen T., Pyhälahti T., Toivanen T., Leito I., Validation of a new measuring system for water turbidity field measurements, *Accredit Qual Assur*, **2014**, 19 (3):175–183
3. Näykki T., Jalukse L., Helm I., Leito I., Dissolved Oxygen Concentration Interlaboratory Comparison: What Can We Learn?, *Water*, **2013**, 5, 420–442.
4. Näykki T., Magnusson B., Helm I., Jalukse L., Väisänen T., Leito I., Comparison of measurement uncertainty estimates using quality control and validation data, *J Chem Metrol*, **2014**, 8 (1): 1–12
5. Näykki T., Virtanen A., Kaukonen L., Magnusson B., Väisänen T., Leito I., Software support for the Nordtest method of measurement uncertainty

evaluation of field on-line turbidity measurement, submitted to *Environ Monit Assess*

6. Näykki T., Leivuori M., Björklöf K., Väisänen R., Laine M., Väisänen T., Leito I., Proficiency test of pH, Conductivity and Dissolved Oxygen Concentration Field Measurements in River Water, *Accredit Qual Assur*, **2014**, DOI 10.1007/s00769-014-1064-5
7. Näykki T., Sara-Aho T., T. Väisänen, Leito I., Application of enriched stable Hg-196 isotope for monitoring the stability of total mercury in water samples submitted to *Int J Environ Anal Chem*
8. Näykki T., The use of silylation for minimizing the interference effects caused by contamination in ultra-low level mercury analytics. *Anal Bioanal Chem*, **2002**, 372 (7): 829-831
9. Näykki, T., Perämäki, P., Kujala, J., Mikkonen, A. Optimization of a flow injection hydride generation atomic absorption spectrometric method for the determination of arsenic, antimony and selenium in iron chloride/sulfate-based water treatment chemical. *Anal Chim Acta*, **2001**, 439 (2): 229–238
10. Näykki, T., Anttila, R., Perämäki, P., Kurikka, A., Nikula, P. Determination of Na₂O from sodium aluminate NaAlO₂, *Talanta*, **2000**, 52(4): 755–760

Rahvusvahelise levikuga aruanded ja konverentsiteesid

Measurement uncertainty revisited: Alternative approaches to uncertainty evaluation, (As a part of Eurolab expert group on measurement uncertainty), *Eurolab Technical Report No. 1/2007, March 2007*

Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories, Magnusson, B.; Näykki, T.; Hovind, H.; Krysell, M., *Report of the Nordtest project 1589-02, June 2003* (revised in 2004 and 2011)

Above mentioned handbook was awarded by CITAC as one the best publication in the world in the field of metrology in chemistry.

Tunnustused

CITAC (Cooperation of International Traceability in Analytical Chemistry) award for one of the best publications in the field of Metrology, **2008**.
Publication: Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories

Administratiivtöö

Juhatusel liige, Finntesting association (merger of Eurolab Finland and Eurochem-Finland associations), **2001–**

Enesetäiendamine

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Omistatud kvalifikatsioon: juhtimise spetsialist

TEEMU NÄYKKI PUBLIKATSIOONID

Publikatsioonid rahvusvahelistes väljaannetes

1. Näykki T., Virtanen A., Leito I., Software support for the Nordtest method of measurement uncertainty evaluation, *Accredit Qual Assur* **2012**, 17:603–612
2. Näykki T., Koponen S., Väisänen T., Pyhälahti T., Toivanen T., Leito I., Validation of a new measuring system for water turbidity field measurements, *Accredit Qual Assur*, **2014**, 19 (3):175–183
3. Näykki T., Jalukse L., Helm I., Leito I., Dissolved Oxygen Concentration Interlaboratory Comparison: What Can We Learn?, *Water*, **2013**, 5, 420–442.
4. Näykki T., Magnusson B., Helm I., Jalukse L., Väisänen T., Leito I., Comparison of measurement uncertainty estimates using quality control and validation data, *J Chem Metrol*, **2014**, 8 (1): 1–12
5. Näykki T., Virtanen A., Kaukonen L., Magnusson B., Väisänen T., Leito I., Software support for the Nordtest method of measurement uncertainty evaluation of field on-line turbidity measurement, submitted to *Environ Monit Assess*
6. Näykki T., Leivuori M., Björklöf K., Väisänen R., Laine M., Väisänen T., Leito I., Proficiency test of pH, conductivity and dissolved oxygen concentration field measurements in river water, *Accredit Qual Assur*, **2014**, DOI 10.1007/s00769-014-1064-5
7. Näykki T., Sara-Aho T., T. Väisänen, Leito I., Application of enriched stable Hg-196 isotope for monitoring the stability of total mercury in water samples submitted to *Int J Environ Anal Chem*
8. T. Näykki, The use of silylation for minimizing the interference effects caused by contamination in ultra-low level mercury analytics. *Anal Bioanal Chem*, **2002**, 372 (7): 829–831
9. Näykki, T., Perämäki, P., Kujala, J., Mikkonen, A. Optimization of a flow injection hydride generation atomic absorption spectrometric method for the determination of arsenic, antimony and selenium in iron chloride/sulfate-based water treatment chemical. *Anal Chim Acta*, **2001**, 439 (2): 229–238
10. Näykki, T., Anttila, R., Perämäki, P., Kurikka, A., Nikula, P. Determination of Na₂O from sodium aluminate NaAlO₂, *Talanta*, **2000**, 52(4): 755–760

Rahvusvahelise levikuga aruanded ja konverentsiteesid

1. Validation of Secchi3000 field analyser for water turbidity measurements. Näykki, T.; Koponen, S.; Leito, I. *Poster in FMTDK conference, March 2013, Tallinn, Estonia*
2. Improving Comparability of Analytical Results with Practical Software for Estimating Measurement Uncertainty. Näykki, T.; Virtanen, A.; Leito, I. *Poster in FMTDK conference, February 2012, Tartu, Estonia*

3. Improving Comparability of Analytical Results with Practical Software for Estimating Measurement Uncertainty. Näykki, T.; Virtanen, A.; Leito, I. *Poster in Eurachem workshop, 6–8 June 2011, Lisbon, Portugal*
4. Measurement uncertainty revisited: Alternative approaches to uncertainty evaluation, (As a part of Eurolab expert group on measurement uncertainty), *Eurolab Technical Report No. 1/2007, March 2007*
5. Nordtest Handbook for Calculation of Measurement Uncertainty Based on Quality Control and Method Validation. Magnusson, B.; Näykki, T.; Hovind, H.; Krysell, M. *Poster in The First International Proficiency Testing Conference, 11–13 October, 2007 Sinaia, Romania.*
6. Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories, Magnusson, B.; Näykki, T.; Hovind, H.; Krysell, M., *Report of the Nordtest project 1589-02, June 2003* Above mentioned handbook was awarded by CITAC as one the best publication in the world in the field of metrology in chemistry.
7. Effects of different pretreatment procedures for analysis of mercury from industrial wastewater. Näykki, T.; Huhtala, S.; Mäkinen, I. *Poster in First Baltic Symposium on Environmental Chemistry. 26–29 September 2001. Tartu, Estonia.*

Muud publikatsioonid

Artiklid erialastes väljaannetes (Soome keeles)

1. Näykki, T., *Laatua laboratoriomäärittäisiin*, Kemia Kemi (2013) 4:52–53
2. Väisänen T., Näykki T., Luotola M. *Ympäristöseurannan menestystekijät tulevaisuudessa – SYKE:n laboratorion rooli*, Vesitalous (2013) 2, Helsinki
3. Näykki, T. *Mittausepävarmuuden arviointi ympäristölaboratoriossa*, Analyysi 2007 44 (4):7
4. Näykki, T. *Ympäristönäytteiden analyysimenetelmien validointi*, Analyysi 2007; 44 (4):6
5. Näykki, T. *Näyteastioiden valinta pienten metallipitoisuuksien määrittämisessä*, Analyysi 2004 41(4):8–13.

Aruanded:

1. Laboratorioiden välinen pätevyyskoe 10/2013. Ravinteet, kloridi, pH, sulfaatti ja sähkönjohtavuus jätevesistä, Kaija Korhonen-Ylönen, Mirja Leivuori, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Ritva Väisänen, Helsinki: Suomen ympäristökeskus, **2014**.
2. Laboratorioiden välinen pätevyyskoe SYKE 7/2013: Talousvesimääritykset, Kaija Korhonen-Ylönen, Teemu Näykki, Mika Sarkkinen, Timo Sara-Aho, Mirja Leivuori, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Ritva Väisänen, Helsinki: Suomen ympäristökeskus, **2014**.
3. Laboratorioiden välinen pätevyyskoe. Uima-allasvesivertailu, Mirja Leivuori, Sami Tyrväinen, Kaija Korhonen-Ylönen, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Helsinki: Suomen ympäristökeskus, **2014**.

4. Proficiency test SYKE 4/2013. Metals in water and sediment, Mirja Leivuori, Kaija Korhonen-Ylönen, Timo Sara-Aho, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas Helsinki: Suomen ympäristökeskus, **2014**.
5. Laboratorioiden välinen pätevyyskoe 1/2013: Uima-allasvesivertailu. Kaija Korhonen- Ylönen, Sami Tyrväinen, Mirja Leivuori, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2013**.
6. Laboratorioiden välinen pätevyyskoe 11/2012. Alkaliniteetti, ravinteet, pH, sähkönjohtavuus ja väri jätevesistä. Kaija Korhonen-Ylönen, Teemu Näykki, Mirja Leivuori, Keijo Tervonen, Sari Lanteri, Ilmakunnas, Markku, Ritva Väisänen. Helsinki: Suomen ympäristökeskus, **2013**.
7. Laboratorioiden välinen pätevyyskoe 3/2013. Katarina Björklöf, Kaija Korhonen-Ylönen, Teemu Näykki, Marketta Turunen, Timo Sara-aho, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Helsinki: Suomen ympäristökeskus, **2013**.
8. Proficiency test SYKE 5/2012. Metals in waters and soil. Mirja Leivuori, Kaija Korhonen-Ylönen, Timo Sara-Aho, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2013**.
9. Laboratorioiden välinen pätevyyskoe 1/2012: Alkaliniteetti, pH, ravinteet ja sähkönjohtavuus luonnonvesistä. Kaija Korhonen-Ylönen, Mirja Leivuori, Teemu Näykki, Olli Järvinen, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Ritva Väisänen. Helsinki: Suomen ympäristökeskus, **2012**.
10. Laboratorioiden välinen pätevyyskoe 2/2012: Uima-allasvertailu. Kaija Korhonen-Ylönen, Sami Tyrväinen, Mirja Leivuori, Teemu Näykki, Olli Järvinen, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Ritva Väisänen. Helsinki: Suomen ympäristökeskus, **2012**.
11. Laboratorioiden välinen pätevyyskoe 3/2012: BOD7, CODCr, CODMn, kiintoaine, Na ja TOC jätevesistä. Kaija Korhonen-Ylönen, Mirja Leivuori, Teemu Näykki, Marketta Turunen, Olli Järvinen; Timo Sara-aho, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Ritva Väisänen. Helsinki: Suomen ympäristökeskus, **2012**.
12. Laboratorioiden välinen pätevyyskoe 4/2012: Happi, a-klorofylli, saliniteetti, SiO₂, TIC ja TOC luonnonvesistä. Kaija Korhonen-Ylönen, Mirja Leivuori, Marketta Turunen, Teemu Näykki, Olli Järvinen, Mika Sarkkinen, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Ritva Väisänen. Helsinki: Suomen ympäristökeskus, **2012**.
13. Laboratorioiden välinen pätevyyskoe 7/2012: Talousvesimäärittelykset. Kaija Korhonen-Ylönen, Teemu Näykki, Mika Sarkkinen, Timo Sara-Aho, Olli Järvinen, Mirja Leivuori, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas, Ritva Väisänen. Helsinki: Suomen ympäristökeskus, **2012**.
14. Proficiency Test SYKE 10/2011: Heavy metals in surface waters. Mirja Leivuori, Kaija Korhonen-Ylönen, Timo Sara-Aho, Teemu Näykki, Keijo

- Tervonen, Sari Lanteri, Markku Ilmakunnas, Helsinki: Suomen ympäristökeskus, **2012**.
15. Verkostomainen yhteistyö ympäristöhallinnon laboratoriotoiminnan menestystekijänä, Marja Luotola, Riitta Pehkonen, Teemu Näykki, Tero Väisänen, Helsinki: Suomen ympäristökeskus, **2012**.
 16. Laboratorioiden välinen pätevyyskoe 9/2011: ravinteet, kloridi, pH, sulfaatti ja sähkönjohtavuus jätevesistä. Kaija Korhonen-Ylönen, Mirja Leivuori, Teemu Näykki, Olli Järvinen, Mika Sarkkinen, Sari Lanteri, Markku Ilmakunnas ja Ritva Väisänen Helsinki: Suomen ympäristökeskus, **2012**.
 17. The effect of gypsum on phosphorus losses at the catchment scale. Petri Ekholm, Elina Jaakkola, Mikko Kiirikki, Kirsti Lahti, Jouni Lehtoranta, Visa Mäkelä, Teemu Näykki, Liisa Pietola, Sirkka Tattari, Pasi Valkama, Ljudmila Vesikko and Sari Väisänen Helsinki: Finnish Environment Institute, **2011**.
 18. Laboratorioiden välinen pätevyyskoe 2/2011: BOD7, CODCr, CODMn, kiintoaine, Na ja TO C jätevesistä. Kaija Korhonen-Ylönen, Mirja Leivuori, Teemu Näykki, Olli Järvinen, Timo Sara-Aho, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas ja Ritva Väisänen Helsinki: Suomen ympäristökeskus, **2011**.
 19. Laboratorioiden välinen pätevyyskoe 1/2011: a-klorofylli, pH, ravinteet, sameus, sähkönjohtavuus ja väri luonnonvesistä. Kaija Korhonen-Ylönen, Teemu Näykki, Olli Järvinen, Mirja Leivuori, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas ja Ritva Väisänen, Helsinki: Suomen ympäristökeskus, **2011**.
 20. Laboratorioiden välinen pätevyyskoe 5/2011: talousvesimääritykset. Kaija Korhonen-Ylönen, Mika Sarkkinen, Teemu Näykki, Timo Sara-Aho, Olli Järvinen, Mirja Leivuori, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas ja Ritva Väisänen Helsinki: Suomen ympäristökeskus, **2011**.
 21. Laboratorioiden välinen pätevyyskoe 7/2010: ravinteet, pH ja sähkönjohtavuus jätevedestä sekä happimääritys rannikko- ja järvisedestä. Kaija Korhonen, Mirja Leivuori, Teemu Näykki, Olli Järvinen, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas ja Ritva Väisänen Helsinki: Suomen ympäristökeskus, **2011**.
 22. Proficiency test SYKE 3/2011: metals in water and sludge. Mirja Leivuori, Kaija Korhonen-Ylönen, Timo Sara-Aho, Teemu Näykki, Keijo Tervonen, Sari Lanteri and Markku Ilmakunnas, Helsinki: Finnish Environment Institute, **2011**.
 23. Laboratorioiden välinen pätevyyskoe 1/2010: alkaliniteetti, ravinteet, pH ja sähkönjohtavuus luonnonvesissä Kaija Korhonen, Teemu Näykki, Olli Järvinen, Mirja Leivuori, Keijo Tervonen, Markku Ilmakunnas ja Sari Lanteri. Helsinki: Suomen ympäristökeskus, **2010**.
 24. Laboratorioiden välinen pätevyyskoe 2/2010: BOD7, CODCr, CODMn, kiintoaine, Na ja TOC jätevesistä. Kaija Korhonen, Teemu Näykki, Olli

- Järvinen, Timo Sara-Aho, Mirja Leivuori, Keijo Tervonen, Sari Lanteri ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2010**.
26. Laboratorioiden välinen pätevyyskoe 4/2010: klorofylli a, saliniteetti, SiO₂, ja TOC luonnonvesistä. Kaija Korhonen, Olli Järvinen, Teemu Näykki, Mirja Leivuori, Keijo Tervonen, Sari Lanteri ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2010**.
 27. Laboratorioiden välinen vertailukoe 6/2010: talousvesimääritykset. Kaija Korhonen, Teemu Näykki, Olli Järvinen, Timo Sara-Aho, Mirja Leivuori, Keijo Tervonen, Sari Lanteri ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2010**.
 28. Laboratorioiden välinen pätevyyskoe 9/2009: ravinteet, pH, sähkönjohtavuus, kloridi ja sulfaatti jätevesistä. Mirja Leivuori, Kaija Tervonen, Olli Järvinen, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas ja Ritva Väisänen. Helsinki: Suomen ympäristökeskus, **2010**.
 29. Laboratorioiden välinen pätevyyskoe 1/2009: a-klorofylli, BOD₇, CODMN, ravinteet, sameus, TOC ja väri luonnonvesistä. Kaija Korhonen, Teemu Näykki, Olli Järvinen, Keijo Tervonen, Sari Lanteri ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2009**.
 30. Laboratorioiden välinen pätevyyskoe 3/2009 BOD₇, CODDCr, CODMn, kiintoaine, Na ja TOC jätevesistä. Kaija Korhonen, Mirja Leivuori, Teemu Näykki, Olli Järvinen, Timo Sara-Aho, Keijo Tervonen, Sari Lanteri, ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2009**.
 31. Laboratorioiden välinen pätevyyskoe 6/2008: metallit vedestä ja lietteestä. Kaija Korhonen, Olli Järvinen, Teemu Näykki, Timo Sara-aho, Raija Ivalo, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2009**.
 32. Laboratorioiden välinen pätevyyskoe 7/2008: talousvesimääritykset. Kaija Korhonen, Teemu Näykki, Olli Järvinen, Timo Sara-Aho, Keijo Tervonen, Markku Ilmakunnas ja Sari Lanteri. Helsinki: Suomen ympäristökeskus, **2009**.
 33. Laboratorioiden välinen pätevyyskoe 9/2008: AOX, pH, ravinteet, sameus, sähkönjohtavuus ja väri jätevesistä. Kaija Korhonen, Teemu Näykki, Olli Järvinen, Lea Kervinen, Keijo Tervonen, Markku Ilmakunnas ja Sari Lanteri. Helsinki: Suomen ympäristökeskus, **2009**.
 34. Laboratorioiden välinen pätevyyskoe 4/2007: metallit ja elohopea vesistä, maasta ja sedimentistä sekä typpi, fosfori, pH, rikki ja TOC lietteestä. Irma Mäkinen, Olli Järvinen, Teemu Näykki, Timo Sara-Aho, Raija Ivalo, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2008**.
 35. Laboratorioiden välinen pätevyyskoe 7/2007: alkaliniteetti, kloridi, pH, sähkönjohtavuus, sulfaatti ja ravinteet jätevesistä. Kaija Korhonen, Olli Järvinen, Teemu Näykki, Tero Eklén, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2008**.
 36. Laboratorioiden välinen pätevyyskoe 2/2007: alkaliniteetti, BOD₇, happi, pH, ravinteet, sameus, sähkönjohtavuus, TOC ja väri. Kaija Korhonen, Olli

- Järvinen, Teemu Näykki, Irma Mäkinen, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2007**.
37. Laboratorioiden välinen pätevyyskoe 3/2007 BOD7, COD, COD, kiintoaine, Na, sameus, TOC ja väri jätevesistä. Korhonen, Kaija, Näykki, Teemu, Järvinen, Olli, Sara-Aho, Timo, Mäkinen, Irma, Tervonen, Keijo, Ilmakunnas, Markku. Helsinki: Suomen ympäristökeskus, **2007**.
 38. Laboratorioiden välinen pätevyyskoe 6/2006. Metallit ja elohopea vesistä ja lietteestä. Irma Mäkinen, Olli Järvinen, Teemu Näykki, Timo Sara-Aho, Raija Ivalo, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2007**.
 39. Laboratorioiden välinen pätevyyskoe 8/2006: alkaliniteetti, kiintoaine, kloridi, pH, sähkönjohtavuus, sulfaatti ja ravinteet jätevesistä. Kaija Korhonen, Irma Mäkinen, Olli Järvinen, Teemu Näykki, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2007**.
 40. Laboratorioiden välinen pätevyyskoe 4/2005: metallit ja elohopea vesistä ja maasta. Irma Mäkinen, Olli Järvinen, Teemu Näykki, Timo Sara-Aho, Raija Ivalo, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2006**.
 41. Laboratorioiden välinen pätevyyskoe 4/2006: a-klorofylli, happi, saliniteetti ja silikaatti (SiO₂) luonnonvedestä. Kaija Korhonen, Irma Mäkinen, Teemu Näykki, Olli Järvinen, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2006**.
 42. Laboratorioiden välinen pätevyyskoe 5/2005: talousvesimääritykset. Irma Mäkinen, Olli Järvinen, Kaija Korhonen, Teemu Näykki, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2006**.
 43. Laboratorioiden välinen pätevyyskoe 6/2005: NNH₄, NNO₃+NO₂, Ntot, PPO₄, Ptot, pH, sähkönjohtavuus ja kiintoaine jätevesistä. Mäkinen, Irma, Korhonen, Kaija, Näykki, Teemu, Järvinen, Olli, Tervonen, Keijo, Ilmakunnas, Markku. Helsinki: Suomen ympäristökeskus, **2006**.
 44. Laboratorioiden välinen pätevyyskoe 7/2006: talousvesimääräykset. Kaija Korhonen, Irma Mäkinen, Olli Järvinen, Timo Sara-Aho, Teemu Näykki, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2006**.
 45. Laboratorioiden välinen vertailukoe 1/2006: ravinteet, sameus ja väri luonnonvesistä. Kaija Korhonen, Irma Mäkinen, Teemu Näykki, Olli Järvinen, Keijo Tervonen ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2006**.
 46. Laboratorioiden välinen pätevyyskoe 1/2005 pH, sähkönjohtavuus, alkaliniteetti, BOD, ravinteet, Na, K, Ca, Mg, happi, TOC, sameus ja väri luonnonvesissä. Irma Mäkinen, Kaija Korhonen, Teemu Näykki, Olli Järvinen, Keijo Tervonen, Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2005**.
 47. Laboratorioiden välinen pätevyyskoe 3b/2004; Epäorgaaniset yhdisteet vedestä. Irma Mäkinen, Olli Järvinen, Kaija Korhonen, Teemu Näykki ja Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2005**.

48. Laboratorioiden välinen pätevyyskoe 6/2004; Talousvesimääritykset. Irma Mäkinen, Olli Järvinen, Teemu Näykki, Kaija Korhonen, Keijo Tervonen, Markku Ilmakunnas. Helsinki: Suomen ympäristökeskus, **2005**.
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